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Preliminary Reports, Memoranda and Technical Notes of the Materials Research Council Summer Conference

La Jolla, California

July 1986

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Department of Chemical Engineering

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PRELIMINARY REPORTS, MEMORANDA AND TECHNICAL NOTES

of the

MATERIALS RESEARCH COUNCIL SUMMER CONFERENCE

La Jolla, California

July 1986

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Foreword

This collection of papers does not constitute a formal reporting of the activities of the DARPA Materials Research Council Summer Conference. Each report, memoranda or technical note is a draft of the author or authors and is their work alone. The Steering Committee, in conjunction with the authors, will decide how this material can best be presented as a formal report to DARPA.

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SUPERLATTICES AND HETEROSTRUCTURES

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R. M. Osgood and M. S. Wrighton

I. OVERVIEW AND MEETING SUMMARY

During the last decade progress in microelectronics has generally proceeded by striving to increase the functionality present on a single chip. This has been achieved by increasing the number of individual devices on a single chip, primarily through the reduction of feature sizes for each device. The success of this approach is measured by the fact that today we have memory chips that store 4Mb (DRAM) and have VHSIC chips with as many as 33M devices (SRAM and DSP) ready for production. The effort to improve the speed and functional throughout have also led to the development of alternative technologies particularly that involving GaAs and HgCdTe based devices, which in many cases rely on heterojunction and superlattice technologies.

The growth of interest in superlattices and heterojunctions is due to two major driving forces, and in addition the important fact that efficient light emitters depend upon the heterojunction quantum well approach. The first major driving force is directed at achieving improved performance in devices as we currently understand them. The goals here are lower noise, higher speed, less leakage current, etc. This effort has led to the high-electron mobility transistor, the heterojunction bipolar transistor, and proposed superlattice infrared detectors. The use of heterojunctions, and in turn superlattices, to provide controlled potential barriers, quasi-alloy properties, confinement wells, and other novel sturctures has spawned the phrase "band-gap engineering." In actual fact, however, thus far we have been able to control material properties in rather few material systems, and neither the successes nor the failures are understood adequately.

The second major driving force for the area of superlattices and heterojunctions stems from the recognition that there are many arguments that suggest the continued growth of functional integration as we know it will end within another decade. Everything we know at present suggests that the current approaches to VLSI, based either on Si or GaAs, will be limited to gate lengths above 0.1-0.25 micron. On the other hand the systems demand for continued improvements in functional integration will not end. Heilmeier (T.I.) has recognized this and argued vigorously for research into new forms of on-chip signal processing that will surpass the gate size limitations. The Japanese have responded to the same problem with a massive MITI program in "New Functional Elements." The payoff for such a program is very great. Yet, corresponding efforts in this country are relatively small. By necessity, they are centered on the technology surrounding heterojunctions and superlattices but not thus far on equally important efforts to develop the technology necessary to pattern structures laterally on the same dimensional scale (~10-100nm) achieved by the vertical growth. These approaches seek to use quantum structures for confinement and reversible quantum mechanical interactions, because of the inherently small size of these structures.

To be sure, quantum structures already are incorporated in today's high electron mobility transistors and quantum well lasers found in most opto-electronic applications. What is needed is the electronic device technology for future systems, in which functional processing is achieved at the molecular device level of integration. Several current approaches center on the fabrication of "quantum dots" in large arrays, in which each dot functions as a localization site for charge in much the same fashion as current devices do. However, the control function, whether it be tunneling or another technique, has not yet been developed. It is apparent that the control function must involve a fundamentally different principle in order to avoid the limitations already foreseen in today's device approaches. This function will surely involve the use of electron wave function phase

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coherence, in analogy with holographic processing in optics. Many questions remain to be answered if this area is to become the post-VLSI technology. The fundamental limits to size and integration must be worked out. Systems considerations such as cellular arrays and/or neural networks have only begun to be suggested: the dominant time constants that govern switching and signal propagation must be determined and questions concerning combined vertical and lateral processing need to be addressed. These and related issues require immediate attention if the exploitation of the ultra-small to achieve higher functional density and functional processing capability is to be incorporated in future systems.

A three day conference (8-10 July, 1986) concerning "Superlattices and Heterostructures" was organized by T.C. McGill and others contributing to this report to address some of these questions. McGill provided a contextual basis for the discussion with an overview that examined some of the common superlattice/heterojunction types: Metal-semiconductor (Al/ZnSe); semiconductor-insulator (Si/CaF$_2$) ; semiconductor-semiconductor (AlGaAs/GaAs; HgTe/CdTe); and nipi doping superlattices. The HgTe/CdTe superlattice for IR detection has the advantages of reliable band gap control, greatly improved device performance, and greater stability. The physical properties have been studied using photoluminescence, electron microscopy, and a variety of other techniques. CdTe/ZnTe is a new optoelectronic material having a lattice mismatch of 6.2%. The strain modifies the band gap of the structure in significant ways. The band gap of InAsSb layers having different compositions can be modified to range between 9 and 12μm. This system is being explored extensively at Sandia. While recent results on the growth have uncovered many problems, the most important may be connected with the small optical absorption and poor transport characterizing these structures. The currently proposed structures have 200 Å of active layer interspersed with 800 Å of strain inducing layer. Thus only

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about 20% of the layers produce optical absorption. Transport normal to the layers may be difficult since the spacer layers have a thickness of 800 Å. Our assessment is that this activity should continue but the likelihood is small that it will produce a near term solution to the requirements for a long wavelength IR detector.

New device structures involving tunneling are of interest because they can be made sufficiently small to guarantee very high speed and packing density. Resonant single and double barrier layers producing negative resistance characteristics are significant not only because of their device potential, but also because they represent sufficiently simple prototypes that a complete physical understanding of their operation should be attainable. Such fundamental insight is of particular importance since it will form the basis for designing new more optimal devices serving a greater variety of functions. In this connection it is to be emphasized that presently existing devices may constitute an intermediate stage preceding the invention of more useful novel quantum devices incorporating some of the many degrees of freedom available for design.

MODFETs constructed form Si/Ge multilayers are regarded as potentially useful devices requiring further exploration. Interest in this system stems from its ready incorporation into standard Si fabricated devices. Furthermore, these devices can be made as MOSFETS and are fast. T.I. is pursuing their development actively.

Metal base transistors using epitaxial silicides ($Si/CoSi_2/Si$) were regarded as promising candidates for near IR space imagery. Because of the relatively low base resistance, these devices would be expected to exhibit high speed.

McGill concluded his overview with a suggested R&D program which includes: (1) growth of necessary structures; (2) study of mechanical properties; (3) development of improved characterization techniques; (4) exploration of novel electronic properties; (5) identification of devices with applications for which they are optimally suited.

This introductory survey was followed by a session on the growth of heterostructures. J. Singh (U. Michigan) discussed theories of heterostructure fabrication technology using MBE by means of sophisticated computer simulations. Such studies provide some insight into the microscopic details of the growth mechanism, subject of course to the validity and relevance of the underlying physical assumptions. R. Dawson (Sandia) reviewed the growth of 3-5 strained layer superlattices including such topics as optimal growth conditions as a function of temperature and deposition rates. A factor of particular importance is the permissible thickness as a function of lattice mismatch. These matters are discussed further in the contribution to this report by J.P. Hirth. H. Morkoc (U. Illinois, Urbana-Champaign) addressed the growth of Si based microstructures. He emphasized that high speed GaAs based devices can now be grown on Si substrates, thereby pointing the way to the achievement of a multicomponent miltipurpose chip which is considered to be an essential ingredient of the "ultimate" electronic technology. Specifically, he stated that remarkably good device performance at both DC and microwave frequencies has recently been obtained from such devices which is nearly identical to the performance achieved in GaAs on GaAs using both direct implant and epitaxial technology.

J.P. Faurie presented a far-ranging discussion of his work concerning MBE growth and properties of the novel 2-6 superlattice systems HgCdTe/CdTe, HgTe/ZnTe, CdTe/ZnTe, and HgMnTe/CdTe. These properties were related by means of a variety of transport measurements including mobility, Hall Effect, and Shubnikov-de Haas osillations to band structure models. He cautioned that interdiffusion between HgTe and CdTe layers cannot be neglected. He attempted to relate the remarkably high hole mobility of $\sim 10^4$ cm^2/volt-sec that he observed in HgTe/CdTe to the presence of interface states--an interpretation that must be regarded as controversial at this stage. The observation of the quantum Hall effect in p-type superlattices is of considerable scientific

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interest since it constitutes the first such observation. Furthermore, he reported on the growth of new 2-6 superlattices: HgTe/ZnTe; HgMnTe/CdTe; and CdTe/ZnTe. Some of these are strained. Faurie is clearly one of the few outstanding practitioners of 2-6 MBE growth in this country and enjoys fruitful collaborations with others both at his institution and scientists at the Ecole Normale Superieure (Paris), CalTech, and Hughes Research Lab. (SBRC). J. Schetzina (North Carolina) is another key contributor to the fabrication and characterization of 2-6 superlattices. His group also enjous widely ranging collaborations, most recently as a major participant in a multi-university URI research effort devoted to DMS (diluted magnetic semiconductor) superlattices. At the conference he reported on his most recent results.

In a session entitled Structural Properties of Heterostructures, J. Hirth discussed the types of defects, most importantly dislocations, that occur in such structures and their influence. His presentation underlined the importance of the active participation of metallurgists in otherwise purely electronic semiconductor activities. (The technology must, in fact, be regarded as , broadly interdisciplinary at many levels involving engineers, chemists, physicists, and materials scientists.) N. Otsuka discussed results of TEM Studies of heterostructures.

The electronic properties of heterostructures were addressed in several presentations. The vexing question of band off-sets in such systems was discussed by D. Wolford (IBM). Since band off-sets between different materials must be known accurately for device applications, it is not surprising that the problem has received wide scientific attention. Unfortunately, there has been little agreement thus far concerning the values of the valence band edge energies on an absolute scale of even such materials as GaAs and AlGaAs. Wolford explained his approach which utilizes pressure dependent luminescence in this system. The values of DE_v as a function of composition

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x in $Al_xGa_{1-x}As$ reported by him appear to be convincing. The same approach should lead to useful results in other heterojunction systems as well.

N-i-p-i doping superlattices were discussed by P. Ruden (Honeywell). The use of doping to modulate the band structure of a single material, like GaAs, by alternating n, intrinsic, and p layers periodically has been explored extensively only recently. The band gaps and hence the optical properties of such structures can be altered very rapidly by light since only electronic and not atomic rearrangements are involved. This suggests a number of applications including high responsivity photodetectors, non linear optical switches, electro-optical switches and modulators, and tunable emitters such as LEDs and lasers.

O. J. Marsh presented an overview of the present state of the Si-Ge heterojunction technology which may well become a leading contender because of its compatibility with the Si technology. The theoretical understanding of the electronic properties of superlattices, which by now is considerable, was surveyed by D.L. Smith (Los Alamos), who has himself contributed substantially to the field. He noted that the presence of strain in non-(100) oriented superlattices induced very large electric fields via the piezoelectric effect. Electric field as high as 10^5 V/cm are easily obtained. These large electric fields could lead to large non-linear optical properties and electrical properties in strained superlattice structures of 3-5 semiconductors such as InAs-GaInAs..

The last topic discussed concerned novel applications of heterostructures. D.K. Ferry (Arizona State and MRC) surveyed electronic device applications of heterojunctions. (Details are reported in Ferry's contribution to this report.)
F. Capasso (Bell Labs) proposed the use of superlattices as low noise photodetectors, an application that shows considerable merit particularly as compared to presently existing avalanche photodetectors. He also discussed lasers and detectors involving

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sequential resonant tunneling, and resonant tunneling transistors. His remarks underline the fact that quantum well structures provide fertile ground for device innovation and that the field may be expected to develop rapidly over the near term. It merits substantial support on DARPA's part, a point made in the recommendations of the group organizing this meeting.

The meeting concluded with presentations by R. Nahory (Bellcove) concerning layered and lateral microstructures, and by M. Derstine (Honeywell) devoted to applications of superlattices as non-linear optical materials. Applications such as optical transistors, optical logic gates, mode locked diode lasers, and reconfigurable optical interconnects were considered in some detail.

In summary, the presentations showed superlattices to be attractive candidates for the next generation electronic and optoelectronic devices for the following reasons: (1) They have low leakage currents and low noise figures thus making them useful for far IR detectors; (2) Tunneling is fast: $\sim 10^{-13}$ for a 100 Å barrier; (3) A tunnel barrier is better as a control functional element than a capacitor; (4) The wavefunction phase becomes available as a means towards "coherent information procession", in principle overcoming the limitation imposed by 0.1 μm gate lengths; (5) Electron transport coefficients can be made larger; (6) They are superior in most respects to alloys as, for example, in the alloy IR sensor HgCdTe as contrasted to the HgTe/CdTe superlattice.

II. RECOMMENDATIONS

Superlattice and heterojunction based projects are found in several DSO supported programs, reflecting their importance in optical sources, non-linear optical materials, electronic devices, and infrared detectors. The total effort, is however, not commensurate with its importance. The significance of these materials to next generation electronics, and its role in maintaining a critical force miltiplier, demands an

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increased investment in the next stage of research, as well as a move of some programs into exploratory development. The total DARPA R&D effort might well be doubled. Several issues must be addressed specifically and are part of these recommendations:

1. Reproducible crystal growth and device fabrication must be sought through well structured experimental development programs. We can currently grow layers on only a few planes, for reasons which are not well understood. Some theoretical programs, well coupled to experimental efforts, could shed light on these limitations.

2. Characterization of materials and device structures becomes far more important as device sizes are reduced. The role of interface properties, such as dislocations and micro-structure, are more important in limiting device performance and need to be better understood.

3. Prototype devices, which illustrate important physical principles, should be fabricated and studied. Presently existing devices may not be optimal, particularly for a jump ahead into quantum-coupled devices. New device concepts must therefore be sought. Continued studies of tunnel structures, both resonant-well and multiple well, are significant for improving scientific understanding.

4. Heteroepitaxy, such as GaAs or Si, should be pursued vigorously. The combinations of materials systems promises to allow optimization of optoelectronics as well as electronics within a single system for high-speed I/O, greater functional on-chip performance, and full wafer integration. The use of Si-Ge, and III-V, strained layers offers other incentives. Studies are needed concerning the role of dislocations, interfacial stability, and incorporation of piezoelectric fields.

5. Lateral patterning is as important as high resolution vertical growth. The next generation of devices (as well as current devices) require definition in all three directions. The program should address electron beam lithograph, focused-ion beam and laser direct writing, and localized implantation.

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6. The study of II-VI microstructures should be pursued because it offers possibilities for making a number of important contributions to the opto-electronics community. Superlattices of HgTe-CdTe continue to show promise for application as IR detectors. Questions such as the degree of inter-diffusion and the precise configuration of superlattices for making detectors have yet to be adequately defined. Recent success in fabricating structures that could act as visible light emitters (p- and n-type CdTe, and CdTe-ZnTe superlattices) have raised the possibility of making II-VI light emitters and detectors and suggests further R&D activity.

7. Several programs in this area are ready for the transition to exploratory development, including:

  a. HgCdTe alloy photovoltaic focal plane arrays

  b. High power quantum well lasers for space-based communications. An early decision on the appropriate wave length (visible or near IR) is required.

  c. Superlattice structures for nonlinear optical functions.

  d . GaAs/Si heteroepitaxial circuits.

III. MATERIALS PREPARATION FOR HETEROJUNCTIONS AND SUPERLATTICES

R. Osgood

Progress in understanding and "inventing" new superlattice structures is tightly tied to the improvements in materials growth. Superlattices must have sharp, smooth interfaces complex chemical compounds, and, thus, growth techniques require an almost unprecedent precise and sophisticated apparatus. Similiarly, the processing of material into working devices requires developing new processing techniques with ultrasmall dimensional control and damage free chemical and physical behavior:

Growth of Superlattice Material

In the last decade, there has been remarkable progress in developing new techniques for the growth of superlattice materials. The two dominant techniques are molecular beam epitaxy (MBE) and metallorganic chemical vapor deposition (MOCVD). The relative strengths and weaknesses of these two approaches are summarized in Table 1. With regard to materials quality, both techniques are capable of growing defect-free, high electrical and optical quality material into sharply defined superlattice structures. Although MBE was historically the first to obtain the abrupt, heteroepitaxy necessary for superlattices. Several researchers have recently shown that two years ago in GaAs/AlGaAs, Angstrom-scale abruptness can be obtained with MOCVD.

Although the bulk of materials growth has concentrated on MBE and MOCVD, other new approaches to epitaxy are under investigation. The primary emphasis in this work is to develop growth techniques which operate at low temperature and yet impart enough surface atom mobility to permit good epitaxy. One of the most intensively explored approaches has been the use optical irradiation of the semiconductor surface during growth. This approach has been examined by Bedhair and Beneking for GaAs, by Donnelly for InP, and Eden and Greene for Ge and Si. In this approach, irradiation

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Table 2. GROWTH TECHNIQUES

MBE
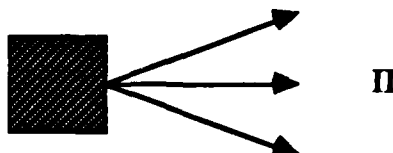
CHARACTERISTICS:

    Ultra High Vacuum
    Flexible
    Slow
    Easy to Control Layer Thickness and Composition

COST: ~$1.5-2.0 Million

ISSUES: Crystal Strain
           Material Defects
           Process Understanding

EXAMPLE OF ISSUE:

    What is the Source of Crystal Defects in MDE Material?

SOLUTION:

    Growth Modeling
    In Situ Dignostics

MOVCD

CHARACTERISTICS:

    Complex Flow and Chemistry
    Fast Growth
    Layer Abruptness Somewhat Harder to Control
    Defect Free Material

COST: ~ $0.5 Million, but $0.5 Million in Safety

ISSUES: insight into Chemistry

with light above the bandgap apparently increases surface mobility and permits very low-temperature epitaxy.

The improvements in developing the technology and techniques for growth have resulted in superlattice structures being grown with a wide variety of materials including II-VI, III-V, and the Group V elemental semiconductors. A partial listing of the materials along with their areas of application are provided by Table 2.

Table 2. <u>MATERIALS GROWN</u>

<u>System</u>	<u>Application</u>
GaAs/GaAlAs	High Frequency Microwave, Digital IC's
InAsSb	Detectors
HgTe/CdTe, ZnTe	Infrared Sensors
SiGe/Si	Integrated Infrared Detectors and Ultrafast IC's
GaAs/Si	Opto-Microelectronic Chips

The III-V materials combinations including GaAs / AlGaAs and InP/InAsP are the most explored materials systems and have been used in several existing electronic and electrooptical devices. However, some of the most impressive recent advances have come in II - VI superlattice materials. MBE grown layers of HgTe / CdTe have been used as a synthetic-materials substitute for HgCdTe alloys. This is a particlularly difficult materials system to grow because of the high vapor pressure of Hg at room temperature. Nevertheless, superlattice structures have been grown with the electrical mobility and bandgap predicted from simple theoretical considerations. One important finding with regard to growth was that the Hg sticking coefficient depended heavily on the substrate

orientation. In addition, the high electron mobility was found to be correlated with a high distribution of interface states.

High-quality, MOCVD-grown II-VI compounds have also been obtained. Two recent results in this area seem particularly promising. First, doped p and n material, in CdTe, has been prepared; this result then allows the formation of an abrupt p-n junction. Work is now progressing to extending II - VI growth to doped ZnSe. This material would be an ideal candidate for a visible-wavelength diode laser - however, the lack of a viable doping technique has thus-far prevented such a laser from being realized.

A third major area of superlattice growth interest is in the merging of the materials, or at least performance, of III - V semiconductors with silicon substrates and materials. In the U.S., the emphasis has been on growing GaAs epitaxially on silicon substrates. The results have been a triumph of the intuition gleaned from many years of MBE growth. In particular, several Japanese and Americans have demonstrated that epitaxial GaAs can be grown on Si, if the silicon substrate is oriented so as to obtain satisfactory lattice match with the GaAs overlayer. Device-quality material has been grown; but dislocations are present and they present a serious problem to using the material for optical devices such as lasers. In a related area, a group in West Germany has used MBE to grow abrupt heterojunctions between SiGe alloys and silicon. MODFET devices have been made with this material, and high mobilities achieved. Note, however, that despite the fact that the mobility is good, it is not comparable to the mobility in GaAs or even, at present, to that in high-quality MOSFETs.

Despite the progress in the developing the technology of MBE and MOCVD, very little has been learned about the basic physics of MBE and MOCVD growth. The physics-oriented studies of MBE growth ceased very shortly after research on MBE materials and devices expanded; MOCVD growth has only recently been subjected to kinetic or physical-chemistry studies.

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With regard to kinetic studies of MBE, Singh has recently begun a Monte-Carlo simulation of the process. The results thus far have, as expected, shown the importance of surface diffusion in controlling surface rough areas. To understand in detail the growth process, it is necessary to have measured a complete set of kinetic rates. Unfortunately, at this time almost none of the kinetic data are known.

No theoretical work has been done on MOCVD growth. In this case, the surface kinetics are more complex, at least conceptually, because of the presence of various partially decomposed precursor molecules.

Experimentally, there have been results which indicate the importance of atomic growth kinetics in MBE. For example, in the case of the growth of As-based systems, it is suspected that the impingement of As_4 on the surface, rather than As_2, species leads to the formation of materials defects. Similarly, as mentioned earlier for the case of II-VI materials efficient atom sticking is typically seen only on certain surfaces - thus, confining epitaxy to specific crystal planes.

Part of the difficulty in conducting experimentation in this area of MBE growth is the lack of readily available probes. RHEED oscillations can be used only to indicate the degree of crystal imperfection of the growing film, TEM and STEM techniques can be used but only ex situ as far as growth is concerned.

Experimental research on the basic physics of MOCVD growth has also been sparse. In P and Si systems have been studied using laser probes of the precursor and product molecules. However, the results have been incomplete and lack any insight into the surface reactions.

Improvements in understanding the physics of crystal growth can be expected to lead to improved materials properties. For example, the problems in atom nucleation have suggested the use of molecular precursors; the result, chemical beam epitaxy, has eliminated many of the nucleation-associated defects. It is clear that future progress in

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both MBE and MOCVD crystal rests on a better understanding of the process physics. The results will be most meaningful if the investigations combine theory and experiment.

Device Fabrication

In silicon integrated circuits, and to a lesser extent in GaAs microwave and digital IC's, circuit fabrication technology has progressed by a series of advances in the scientific issues important in microfabrication and the discoveries or inventions of new fabrication techniques, such as x-ray lithography, or rapid thermal annealing. With a few exceptions, principally the growth techniques mentioned above, the development of microfabrication techniques for superlattice materials has been haphazard.

There are two basic issues in processing superlattice material: lateral patterning and the development of damage-free processing. The very thin layers in superlattice structures set the scale-size for the smallest devices, i.e. ~ 200-1000Å. For device applications, the ability to pattern latterally on this scale size is as important as the vertical definition of the material layers. In addition the thin layers, many times of soft materials, coupled with the interfacial strain mean that extreme caution must be observed in any processing step or materials damage will result.

The techniques being developed for VLSI and ULSI are to first order applicable for submicrometer lateral processing, that is to say, although processing damage may result, techniques such as x-ray lithography can be used to produce hundreds-of-angstrom-scale devices; e-beam lithography would be required to produce the original mask. The most difficult new problem presented by superlattice structures is that high resolution must be maintained or accomplished through many vertical layers.

With regard to the development of damage-free techniques for fabrication, there is essentially no existing organized research program for superlattice materials. The most important needs are 1) to develop low-temperature processing, to prevent layer interdiffusion and external stressing, and 2) to develop damage-free processing which

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can be used _in situ_ during or between growth steps. The _in situ_ condition allows the patterning and alteration of the material without altering the pristine surfaces. At present the _ex situ_ techniques of wet etching and lithography can be used but with almost unavoidable surface contamination. _In situ_ techniques for MBE doping have been examined, which are based on high-resolution focused ion beans. However, material damage is an unavoidable consequence thus far. Application of _in situ_, rapid thermal annealing may help ameliorate the damage. As mentioned above, damage-free optical techniques appear suitable for _in situ_ patterning of MOCVD grown material.

Finally, in this section we have thus far pointed out that fabrication of superlattice structures presents particularly difficult new problems. In fact, the unique superlattice structure also allows some very interesting new device structures to be fabricated. For example, using a materials'-sensitive (wet) etch stop technique, very thin GaAs and Si membranes have been made for micromechanical sensors. Similarly, the work by Petroff on fabricating quantum wires is based on a damage-induced diffusion sequence, which is unique to superlattice materials.

In conclusion, there has been essentially no organized research program on developing new fabrication concepts and technology for superlattice materials. The realization of new-device-concept prototypes and the manufacture or development of IC's based on superlattice structures will be hampered or even prevented without development of fabrication techniques.

IV. DEVICE CONSIDERATIONS FOR SUPERLATTICES AND HETEROJUNCTION STRUCTURES

D. K. Ferry

The concepts of "band-gap engineering" have become important primarily for their impact on performance modifications of semiconductor devices and for their suggestion of new methods of device operation. These two thrusts become the important driving forces for continued efforts in these directions. Firstly, the ability to modify material characteristics through alloying, and through the use of superlattices and quantum wells, allows us to tune energy gaps, and hence electrical and optical properties. Thus, we may optimize device structures to provide higher frequency, lower noise, faster switching, better responsivity, etc.

Secondly, the use of superlattices and heterojunctions opens the door to new types of devices. New, close-coupled structures may provide different methods of controlling, and processing, information. This, in turn, may allow continued growth in density of single integrated circuits. In fact, this area must be one of the most important in producing the next generations in electronic devices and systems.

Current Devices

In current devices, heterojunctions can be used to improve control over carrier dynamics. In the heterojunction bipolar transistor, the emitter is provided from a wider band gap material than the base. This presents a larger barrier to hole injection from the base to the emitter (leakage) than for the desired electron injection from the emitter into the base. This is a more effective way of optimizing the injection ratio than using simple doping control as is done in Si bipolars. The injection ratio is only linear in the doping ratio between emitter and base, while it is exponential in the potential barrier height. With the injection ratio controlled by the barrier height, doping levels can now be chosen to optimize other device parameters.

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In the high electron mobility transistor, the heterojunction between the substrate (e.g., GaAs) and the modulation-doped layer (e.g., GaAlAs) provides for electrons to move from the latter into an interfacial inversion layer, Fig. 1. The resulting structure now allows MOS-like behavior in a high speed material like GaAs. Complementary symmetry (p-channel and n-channel devices) can be achieved to provide the low power dissipation found in CMOS circuits, while maintaining the high speed. In microwave applications, the reduced dimensionality of transport in the inversion layer provides lower noise operation in amplifiers than is achieved in MESFET devices.

Regular arrays of heterojunctions provide superlattices which yield additional controls over the effective band gap of the composite material. In HgTe / CdTe superlattices, for example, an effective band gap (due to quantization in the potential wells) can provide a band-gap variability comparable to that of the alloy. This is shown in Fig. 2. Preliminary measurements have confirmed this variability, and early work on detectors at Texas Instruments indicates good results in fabricated detectors.

Heterojunctions and superlattices on Si are now being investigated as well. GaAs and CdTe have been grown on Si, and, in fact, GaAs and Si devices have been fabricated together on one heteroepitaxial wafer. Strained layers of Si-Ge alloys have also been grown on Si substrates for the purpose of producing Si HEMTs. However, these devices are not expected to be superior to normal MOSFETs. Rather, the precise doping control achievable in MBE growth promises more usefulness for Si FIR detectors and for nipi superlattices, which also have some useful properties for detectors and as nonlinear optical material. There are also possibilities for light emission from these superlattices.

The superlattices offer the additional opportunity in these devices to differentiate the transport in the direction normal to the superlattice from that parallel to the layers. Thus, we can control the transport normal to the layers, while maintaining good transport
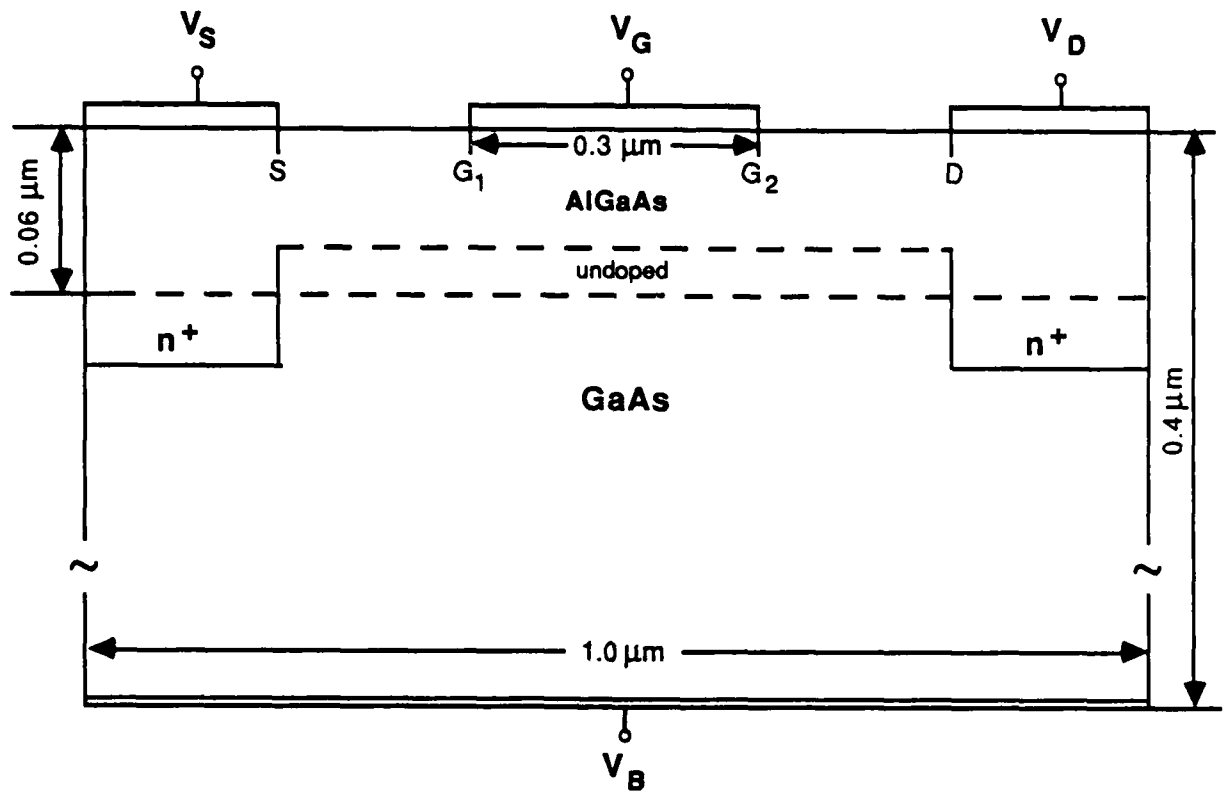
Figure 1(a). The High Electron Mobility Transistor.
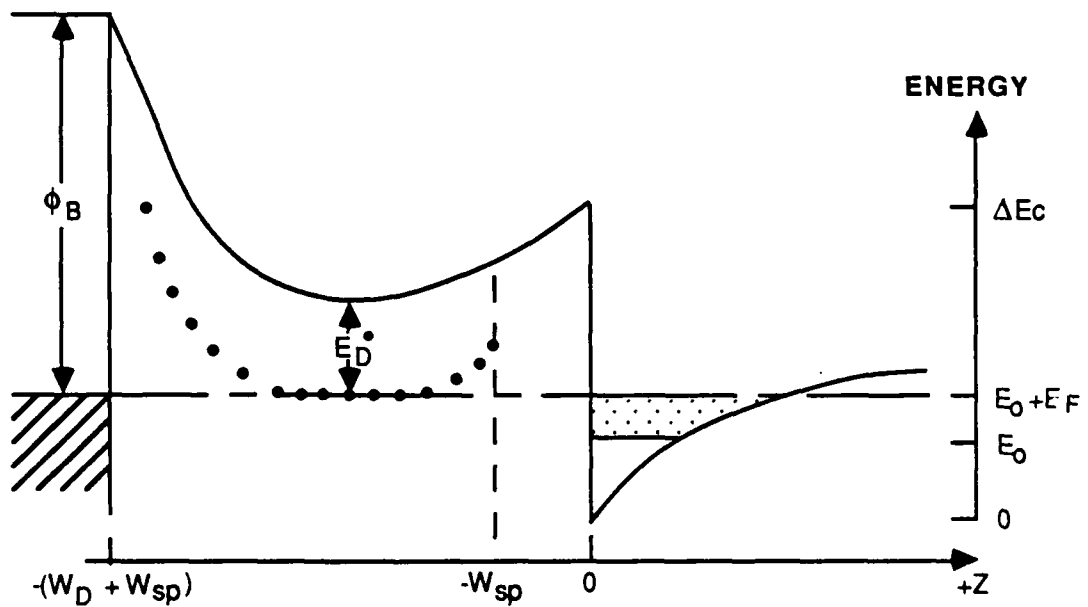
Figure 1(b). Potential variation through gate region.

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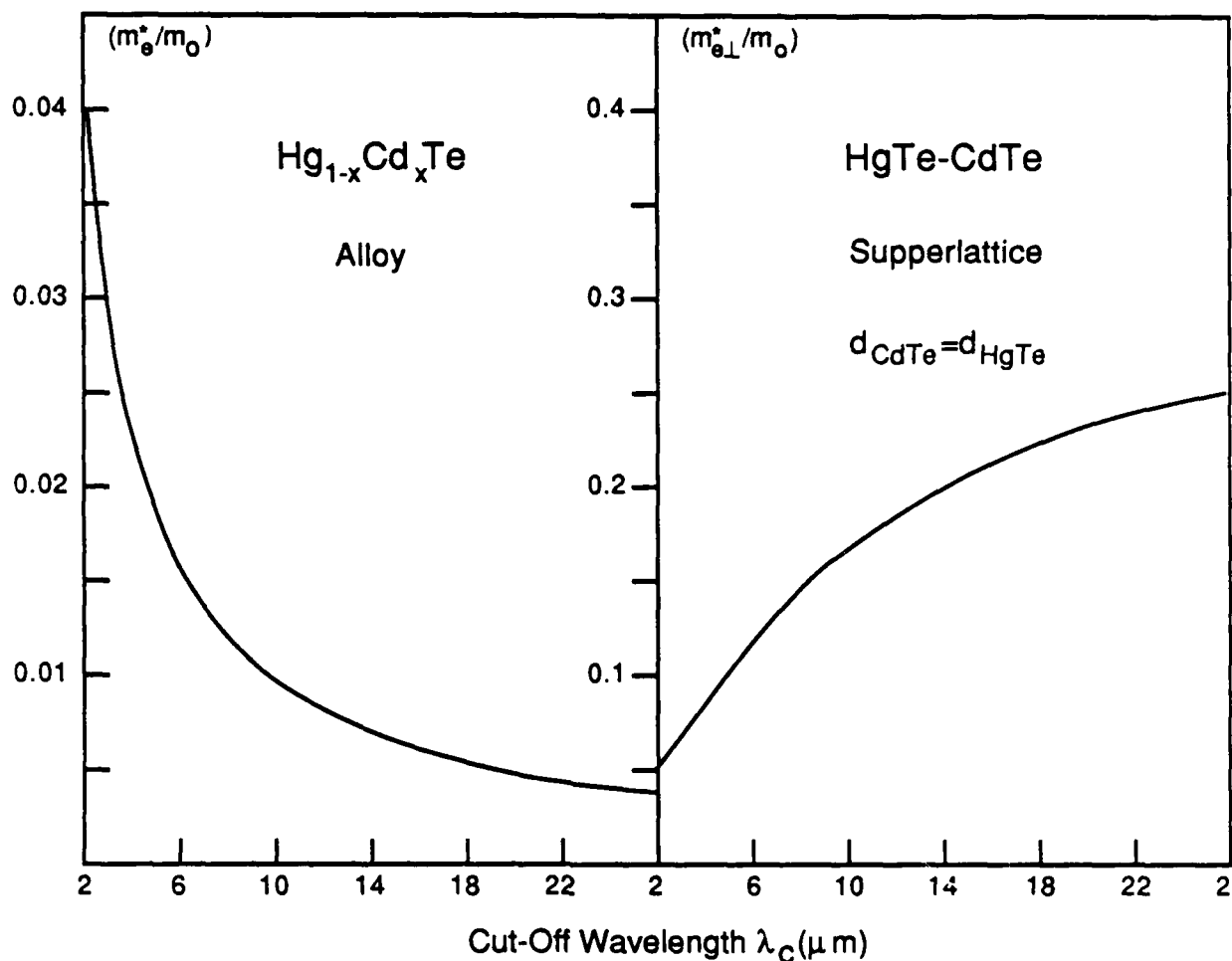
Figure 2.   Cut-off wavelength for superlattices and alloys of HgTe and CdTe.

parallel to the layers. This arises as a result of the quantum structure of the superlattice, and is particularly important in optical devices.

Future VLSI

The driving force for continued growth in VLSI complexity is increased functionality per unit chip area. This implies that each new generation of microchip provides a major step forward in functional capability. Yet, there are major concerns now being voiced by competent scientists and engineers that this growth in complexity might be ending. We are currently utilizing approximately 1μm gate lengths in present VLSI, while the coming generation of VHSIC chips will have 0.25-0.5 μm gate lengths. The

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major concerns are that a combination of lithography, failure of scaling, and interconnect problems will limit current VLSI approaches to gate lengths in the 0.1-0.2 μm regime.

In order to push beyond this barrier, we must find new types of devices, and construct new methods for inter-device communication, since we can no longer allow ourselves the luxury of infinitely many metal interconnect lines. Heilmeier (Texas Instruments) has compared this area to biologically motivated electronic circuitry and has pointed toward quantum coupled devices (QCDs). The Japanese have followed with a MITI program in "new functional elements."

These new functional chips can be conceived of as massive arrays of QCDs onto which are mapped highly parallel architectures. The nature of these architectures and their local properties (for small groups of QCDs) are not known at present. On the other hand, we know little about possible mechanisms by which individual QCDs can communicate and about how these communication channels can be controlled. However, tunneling is one likely mechanism for these interactions.

Tunneling has been investigated in a number of device structures that are appropriate to QCDs. Single resonant tunneling diodes have been fabricated and tested in the past years. These have exhibited oscillations into the microwave range and have exhibited negative resistance at 2.5 THz. Multi-quantum well tunneling has also been observed, and tunneling negative resistance has been incorporated in a HEMT, yielding a three-terminal device. These studies are providing significant information about tunneling which can ultimately be utilized for QCDs.

If this area is to provide the needed future generations of electron devices for continued growth in VLSI functionality, then extensive research is needed now. QCDs require not only good growth of heterostructures, but also high resolution lateral patterning capabilities. While extensive work is underway on the materials growth, relatively little is being pursued for the high resolution lateral patterning required. On the

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other hand, a great deal of systems work is underway, some of which may prove useful for this area. It is important to understand how these architectures may be mapped onto QCD, and develop an understanding of the fabrication and properties of them.

V. MATERIAL PROPERTIES AND CRYSTAL DEFECTS IN STRAINED SUPERLATTICES

J. P. Hirth

For satisfactory electrical and optical properties, strained layer structures must have mechanical integrity, must remain defect free at the interfaces, and must have controlled intergradation at interfaces, all involving crystal defects. The status of understanding of these topics is outlined.

Crystal Growth

a. Computer simulations are useful guides, particularly if operated in an interactive mode with a crystal growth group. One must bear in mind that model materials, not real materials, are being studied to demonstrate trends in behavior. Demonstrations of ledge growth versus island growth date from the 1950's. For the SSL field, work with covalent-type many body potentials is needed. Of particular interest would be the paired study of both island and ledge type growth of A on B together with B on A, since surface energy balances inevitably indicate that wetting will be more difficult for one of the two situations.

b. For either island or ledge type nucleation and growth from vapor phase, nucleation theory and experiment (mainly for metals depositing on inorganic substrates) show that intermediate substrate temperatures and low vapor phase supersaturations favor defect-free growth. At low temperatures or high supersaturations, heterogeneous nucleation of crystals with interface stacking faults or dislocations become about as favorable as homogeneous nucleation. For the island growth case, growth at intermediate temperatures or heating to intermediate temperatures at the island coalescence stage can lead to the annealing out of some defects.

c. Extensive studies by ledge decoration techniques have verified the pervasiveness of the surface diffusion, terrace, ledge, kink model of growth. Ledge

spacings are determined by diffusive interactions and give an indirect indication of surface diffusivity. Recent work has demonstrated electrostatic charges on ledges in ionic crystals and associated external electrostatic field effects on ledge growth for ionic crystals. Such fields could have consequences for electronic materials, particularly for the II-VI compounds with their partially ionic character and possibly for the difficult {III} crystal growth.

d. The estimation of the critical thickness for spreading of dislocations along the interfaces of layer structures (Matthews and Blakeslee) provides a lower bound for the thickness above which growth of a perfect SSL is not possible. Calculations using full anisotropic elasticity show that the simpler isotropic elastic result is correct within ~ 20 percent. Frictional glide resistance (Peierls stress) would tend to increase the critical thickness.

e. Overgrown ledges tend to trap dislocations at the consequent imbedded interface as demonstrated for GaAs on Si. On nominally flat {100} interfaces the same effect can lead to damage. As shown in Fig. 1, the ledge growth mechanism leads to sets of ledges of opposite sign. When these trap dislocations of opposite sign they relieve interface strain locally. However they also lead to opposite sign rotations of the overgrown crystal, producing a disclination with a large local elastic strain field. As the layer thickens, strain relief by cell wall formation or microcracking should occur. The resulting configurations, Fig. 1, closely resemble those sometimes observed experimentally.

f. For crystals with lower symmetry than cubic, dislocations with larger rotations can be formed in order to prevent antisite defect type antiphase boundaries. In cubic crystals similar defects can occur locally between adjacent unit ledges. The elimination of the latter defect can lead to interface dislocation generation.

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(a) disclinated

(b) relaxation
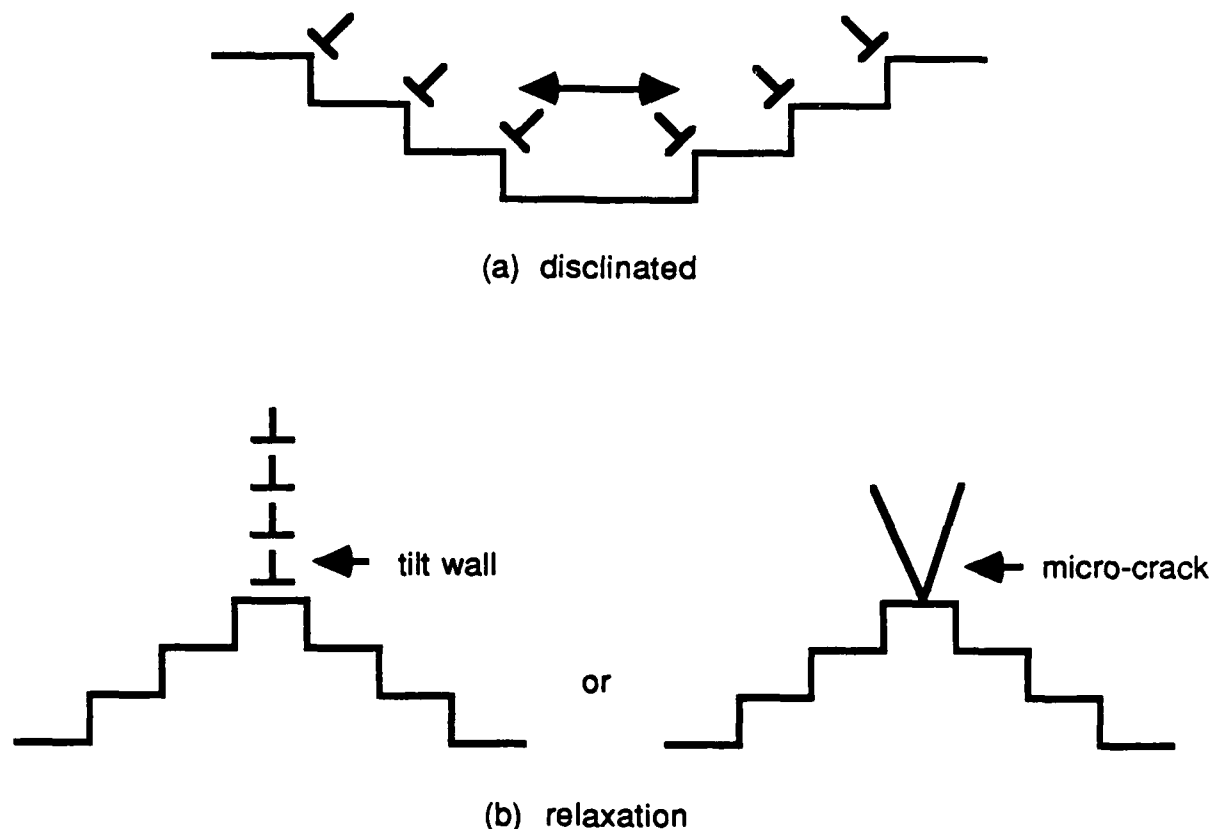
Figure 1. Dislocation - ledge - dislocation structures. Double arrows indicate disclination rotation.

Interface Stability

Once grown as a perfect crystal array, a SSL remains vulnerable to damage by dislocation injections or microcracking. The most vulnerable sites are at lateral free surfaces normal to the interface layers. Detailed calculations show that in the absence of external stress, the critical thicknesses for injection of such defects exceed those for dislocation spreading mentioned previously, so the latter still serve as lower bound estimates. Vulnerability increases with increasing external stress, layer thickness, and lattice mismatch and in the presence of external stress the critical thickness can become less than the value for dislocation spreading.

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Interdiffusion Effects

a. Enhanced Diffusion

Image forces arising from elastic incompatibilities act on dislocations near free surfaces and interfaces. These cause climb and attendant vacancy emission that can produce vacancy supersaturations and enhanced diffusivity. In metal systems the effect has been demonstrated to produce diffusion enhancement by factors up to 10^6.

b. Dislocation Injection

Interdiffusion leads to climb forces on intrinsic or extrinsic interface dislocations. These cause the injection of the dislocations from the interface into the adjacent crystals and ultimately to tilt wall (subgrain) formation.

c. Suppressed Diffusion

Almost exclusively, tabulated interdiffusion coefficients were measured for crystals containing large numbers of dislocations and grain boundaries. These act to maintain near local equilibrium vacancy concentrations and permit both unbalanced fluxes of A and B interdiffusing species and Kirkendall marker shifts. For SSL interfaces, the only vacancy sources and sinks are at free surfaces. Hence, local vacancy chemical potentials can be sustained and the local fluxes of A and B must be nearly equal and opposite. Thus the interdiffusivity will be controlled by the slower diffusing species and will be less than tabulated values.

Status Table

As some indication of status and research needs the following table is presented. The numerical scale is such that 1 indicates extensive work or understanding and 5 indicates none. For priority, 1 is the highest.

Effect	Development of Theory	Experimental Characterization		Priority for Research Need
		Inorganic Crystals and Metals Semiconductors	Elemental and Compound	
1. Crystal growth				
a. In situ TEM study of island growth	2	2	5	4
b. Decoration study of ledge growth	1	2	5	2
c. Growth as function of temperature, supersaturation, electric field	2	2	3	2
d. TEM, X-ray characterization	1	1	2	ongoing
e. Verification of critical thicknesses	2	2	4	3
f. Studies of origin of defects	3	2	4	2
g. Role of disclinations	3	4	5	4
2. Interface Stability				
a. Dislocation injection	2	5	5	2
b. Microcracking	2	5	5	2
c. Integral Mechanical Properties	3	5	5	2
3. Interdiffusion Effects				
a. Climb enhanced diffusion	2	2	5	4
b. Climb induced dislocation injection	2	3	5	4
c. Diffusion suppression by lack of vacancy sources-sinks	2	4	5	5

REFERENCE GUIDE

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   b. Ledge decoration: G. Bassett

   c. Island growth: J. Mentor, D. Pashley, M. Stowell.

   d. Critical thickness: J. Matthews, E. Blakeslee.

2. Interface Stability

   a. A. Evans and J. Hirth, 1985 DARPA Report, J. Appl. Phys., in press.

3. Interdiffusion

   a. Enhancement and climb: K. Shinohara.

VI. RELATIONSHIP OF INORGANIC SUPERLATTICES AND ORGANIC MULTILAYERS

Mark S. Wrighton

Superlattice structures of semiconductor materials grown by MBE or MOCVD have sparked much interest in solid state physics. The issue addressed here is the relationship of such structures to analogous structures derived from discrete molecules. Interesting electronic structural features of a superlattice consisting of alternating layers of wide and narrow gap semiconductors (e.g. GaAs; $Ga_xAl_{1-x}As$) stem from the fact that the layer thicknesses are extremely thin, tens of Angstroms, for example. The small layer dimension results in certain "quantum effects" that, in principle, can be exploited to produce new kinds of electronic devices. Unarguably, the superlattice structures result in properties unattainable from a homogeneous distribution of the constituent atoms, and may also serve as the basis for better devices. As an example, band gap engineering for IR detector devices based on $Hg_xCd_{1-x}Te$ appears to be easier with superlattice structures than when using alloys. The small dimension associated with the layers of superlattices gives rise to quantum effects and extension of this concept to higher dimensionality can be effected by fabricating structures such as quantum wires, or boxes where, for example, carriers in a semiconductor may be constrained to occupy a volume defined by energy barriers placed fifty Angstroms apart. At least superficially, there appear to be molecular analogues of semiconductor superlattices, quantum wires, and quantum boxes. In some respects the molecular "quantum systems" are better developed than semiconductor systems. Molecular systems are more easily fabricated and represent systems where more precise control of dimension is possible. The three sections that follow outline the relationships between molecular and inorganic solid superlattices, quantum wires, and quantum boxes.

Superlattices

The magnificent layered structure of semiconductor superlattices is also found for multilayers of organic molecules assembled by the Langmuir Blodgett techniques developed a half century ago, Figure 1. The layer thicknesses of the semiconductor superlattice must be sufficiently small that quantization effects can be found, in order to realize the unique properties associated with superlattices. In the case of the organic superlattice, also shown in Figure 1, the unique properties stem from the ordered arrangement of molecular units. It is clear that each of the two systems illustrated in Figure 1 can be characterized as systems having a great deal of structural order, consisting of layers of ordered materials. The tail-to-tail arrangement of long chain fatty acid molecules is a prototypical bilayer structure that can have a close-packed arrangement of the molecules in each layer. Such monomolecular layers can be regarded as 2-dimensional crystals with a thickness that depends on the length of the hydrocarbon tail, $CH_3(CH_2)_n$- of the fatty acid, $CH_3(CH_2)_nCOOH$. Assuming that there are applications of highly ordered organic monolayers and multilayer assemblies an important issue is whether the order can be made to extend over large dimensions. It is an established fact, though, that over significant dimensions, high order can be achieved for monolayers and multilayers. Perfection of semiconductor superlattices, in terms of structure, is also an established fact and has led to the ability to do fundamental physics experiments that reveal the unique properties of the superlattice assemblies. The point is that both organic superlattices and semiconductor superlattices can be prepared with sufficient perfection that investigation of the properties can be undertaken.

The structural similarities of organic superlattices and semiconductor superlattices do not necessarily give rise to similar properties. Semiconductor and organic superlattices both have unusual electronic and optical properties, but there are fundamental distinctions that suggest that different uses will be made of the

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(a)

(b)

Polar Head
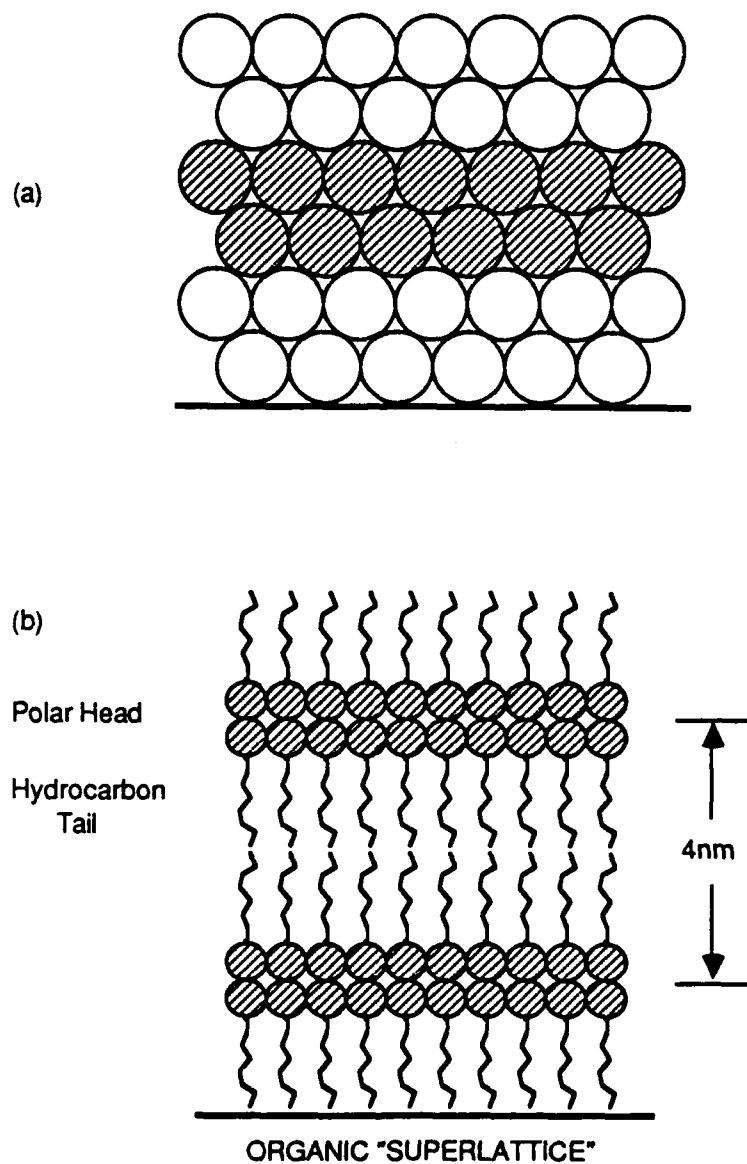
Hydrocarbon
Tail

4nm

ORGANIC "SUPERLATTICE"

Figure 1. (a) A semiconductor superlattice and (b) an organic "superlattice" consisting of a multilayer assembly of long chain fatty acid molecules having an insulating hydrocarbon tail, $CH_3 (CH_2)_n$-, and a polar head, -COOH.

materials. For example, the semiconductor materials can have very high carrier diffusion coefficients whereas organic molecules are not typically associated with large diffusion coefficients. In fact, many potential applications of organic superlattices would depend on their insulating and protective properties. Organic superlattices have some "functional" properties that depend on the hydrocarbon tail that is also apparently crucial in bringing about order.

The tail of the monolayer-forming molecules are typically insulators and this electrical characteristic gives rise to the suggestion that organic superlattices comprise thin, uniform, dielectric films that can be useful in a MISFET device, for example, as the insulator layer. Close-packed monolayers can also be regarded as potentially useful as barrier films. In a rough analogy to insulating tails of organic molecules, intrinsic semiconductor superlattices can play a role in achieving the properties of the completed assembly as in the n-i-p-i superlattices where the i layers contribute to the properties that could give rise to very sensitive photodetectors. The head groups of the monolayer forming molecules can be varied over a wide range and a variety of experiments having been done that show that (1) electronic energy transfer occurs among the head groups of a single layer and (2) electronic energy transfer and electron transfer can occur across layers from one head group layer to another. The point is that the head group can be varied to bring about interesting electronic structural features. Indeed, there appears to be some analogy between the interaction of quantum wells in a semiconductor superlattice and the interaction of head groups in the organic superlattice. The difference is that the quantum effects in the semiconductor stem from the thin layers of semiconductor, say fifty Angstroms of GaAs bounded on either side by layers of wider gap $Ga_xAl_{1-x}As$. The quantum effects associated with head groups of the organic superlattices generally stem from the small (molecular) size of the head group itself. The interactions of the head groups in a layer are analogous to the interactions of molecules

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in a molecular crystal. The point is that the head groups interact modestly in comparison to the units of GaAs in a 50Å layer. The transport of carriers in the GaAs layer is expected to be associated with large diffusion coefficients, whereas organic head groups would not be expected to have good carrier transport properties. Thus, in a semiconductor superlattice of n-i-p-i layers functioning as a photodetector the carriers can be swept along the layers, in principle, to give a fast and sensitive device. Thus, there is a way to overcome the relatively slow carrier transport perpendicular to the layers of the semiconductor superlattice. While similar structures could be envisioned in the organic superlattices, photogeneration of carriers is inefficient in molecular systems, and even if generated the carriers could not be rapidly collected in the lateral dimension. Finally, the n-i-p-i structure in the semiconductor materials illustrates another fundamental difference: the n-i-p-i structure can be designed in a way that yields photoresponse (carrier generation) at longer wavelength than the wavelength associated with the band gap of the pure semiconductors. In contrast, the head groups of the organic molecules will not interact across such a large dimension and "cooperative" properties do not emerge. The wavelength response would typically be characteristic of the pure head group.

The organic superlattices and semiconductor superlattices have some obvious structural similarities. Differences in electronics properties occur because the molecular entities do not have delocalized electronic structures in the sense of semiconductors such as GaAs or Si. The wave functions that describe the molecular system are more tightly confined than for the semiconductor, for most of the monolayer forming molecules. These considerations suggest that head groups that are known to form conducting crystals or polymers might provide interesting research opportunities. However, it should be appreciated that forming highly ordered, two-dimensional conducting crystals or polymers by reactions of head groups is likely to be difficult due to the geometrical

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demands of such processes. While polymerization of head groups has been demonstrated it is not clear that the degree of polymerization is large and there is no compelling evidence that highly ordered materials result. Nonetheless, the analogy between organic and semiconductor lattice could be made more extensive in situations where the head groups could be involved in situations like TTF-TCNQ (conducting crystals) or polythiophere (conducting polymer) were extensive delocalized electronic structures obtain, Figure 2.

Quantum Wires

A quantum wire can be regarded as an object to confine carriers that is long but small, say tens of Angstroms in the other two dimensions, Figure 3. There is obviously the prospect of effectively producing such structures in semiconductor materials by a variety of procedures including applied external perturbations or ultrasubmicron fabrication techniques. From the molecular perspective, a wide variety of "quantum wires" can be synthesized. The term "molecular wire" has been used by researchers engaged in the synthesis of models of the primary units of the natural photosynthetic apparatus. A molecular quantum wire can be taken to be a long-chain, conjugated molecule such as the polyphenylene illustrated in Figure 3. Such a molecule is long in comparison to the diameter of the cylinder defined by the system. A hole or electron introduced into such a molecule can be regarded as delocalized over the entire molecule. A large number of quantum wires like polyphenylene can be envisioned and arguably their size and electronic properties can be better controlled than quantum wires "carved" from semiconductors or conventional metal. At this point it is not clear that molecular synthesis can yield wires which are as rigid or as long as can be envisioned with semiconductors, but there is no fundamental barrier to achieving long molecules. Arrays of molecular quantum wires could, in principle, be doped into organic matrices in

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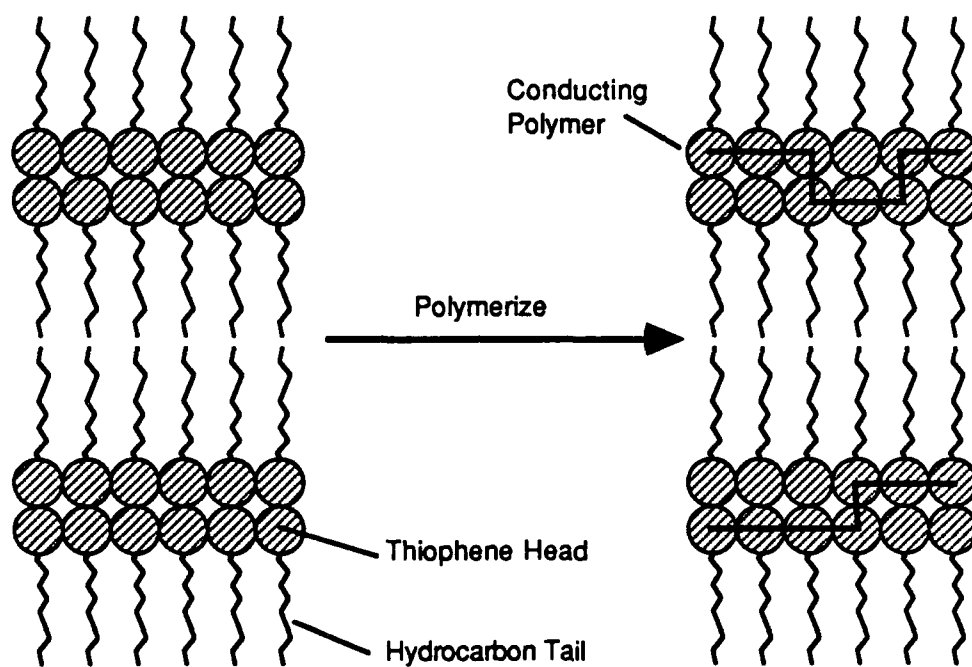
Figure 2. Polymerization of thiophene head groups to produce a layer of relatively highly conducting material between the insulating hydrocarbon $CH_3(CH_2)_n$- layers.
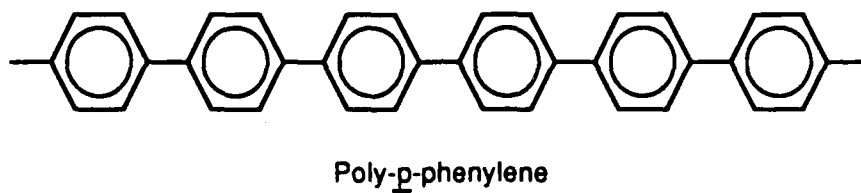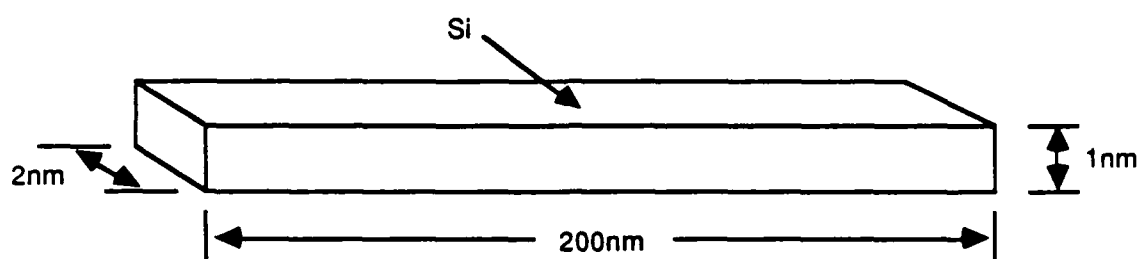
Figure 3. (a) A semiconductor quantum wire and (b) a molecular quantum wire.

a manner that gives a degree of order, Figure 4, where the matrix material has energy levels that more or less insulate the quantum wires from each other.

The semiconductor quantum wires and molecular quantum wires are more rigorously analogous than are the semiconductor and organic superlattices. The structural and electronic analogy is extensive and molecules can be made smaller and more well-defined. Whether useful applications can be derived from quantum wires remains to be seen, but the molecular approach here cannot be easily discounted. The virtue of the semiconductor quantum wires derives from the fabrication of the quantum wires in, or on, a matrix which is perceived to be potentially useful in both electronics and optical applications. The ability (or inability) to interface the molecular quantum wires with real "wires" to produce molecular electronics devices is a key issue that must be resolved. There are clearly sensor functions unique to molecular materials, but whether there are other achievable applications associated with the quantum wires (semiconductor or molecular) is not presently resolved. It would seem that new concepts for interfacing quantum wires with the macroscopic world are needed; exploitation of the wave properties of electrons may represent a significant opportunity.

Quantum Boxes

A quantum box can be regarded as a three dimensional object for confining carriers where all three dimensions are small, say less than fifty Angstroms. Molecules, or even isolated atoms, represent the ultimate quantum boxes. Indeed there is a discrete molecule with the shape of a cube, cubane, of the formula C_8H_8, Figure 5. Molecules can be synthesized with a wide range of geometrical and electronic structure. Some structures based on fused aromatic rings are included in Figure 5. The molecular quantum boxes are very well-defined, easy to prepare, manipulate, and characterize. Indeed, molecular quantum boxes are far more advanced than semiconductor quantum boxes. Molecules can be placed in an ordered arrangement into matrices and have
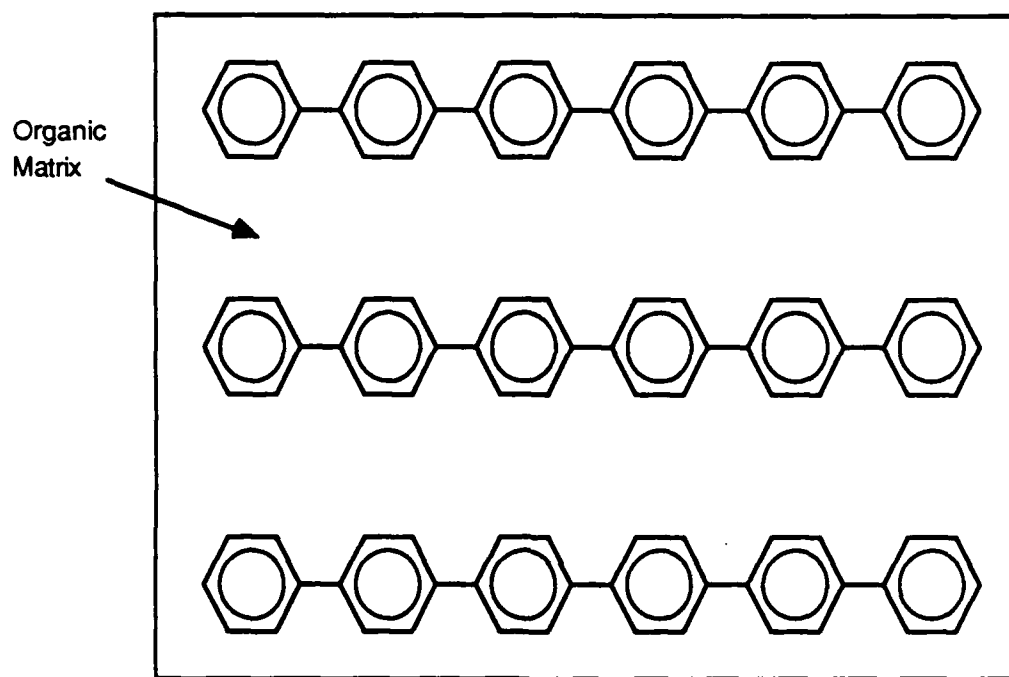
Figure 4. Molecular quantum wires in an ordered arrangement in an organic matrix.
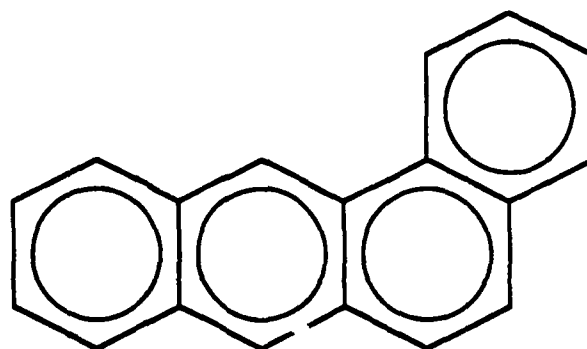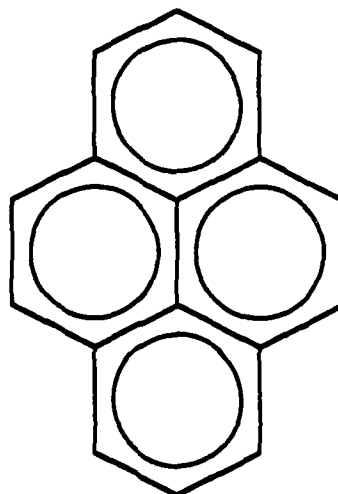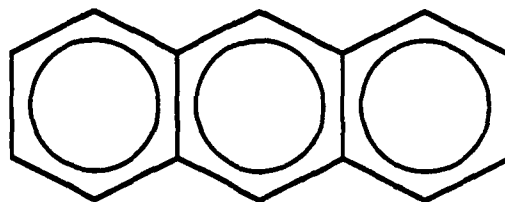
Figure 5. Some examples of molecular quantum boxes.

been elaborately characterized spectroscopically. Physicists studying quantum boxes may profit from the considerable knowledge already accumulated in connection with molecular quantum boxes. As with quantum wires, new concepts for interfacing quantum boxes with the macroscopic world are needed and exploiting optical properties of arrays of quantum boxes and wave properties of electrons represent opportunities.

<u>Summary</u>

Molecular and semiconductor (or other inorganic solid) materials can be used to produce structures that have at least one dimension which is sufficiently small that quantum effects can be expected. By virtue of the electronic structure of semiconductor materials such as Si and GaAs there appear to be truly unique properties associated with semiconductor superlattices that suggest important applications in electronics or optics. Molecular superlattices have a different set of properties with associated potential applications that, include, but extend to areas outside electronics or optical devices. Quantum wires and quantum boxes are structures that are not only geometrically similar for molecular and semiconductor systems, but also strictly analogous electronically. Indeed, it is possible that molecular quantum wires and boxes offer more: they can be prepared by the techniques associated with molecular synthesis, the sizes can be varied and controlled precisely, and a wide range of geometrical, optical, and electronic properties can be rationally designed and prepared. The applications for semiconductor quantum wires and boxes are not agreed upon; for now such quantum structures deserve attention at the basic research level and many exciting physics experiments can be undertaken to fabricate and characterize them. As these physics experiments proceed an attempt should be made to make an assessment of the distinctions between the molecular systems and those derived from inorganic solids. The distinctions will likely define the unique applications of each of the materials systems.

AGENDA

SUPERLATTICES AND HETEROSTRUCTURES

July 8-10, 1986
La Jolla, CA

ORGANIZERS:
    MRC: H. Ehrenreich, D. K. Ferry, J. Hirth, T. McGill, R. Osgood
    DARPA: J. D. Murphy, J. Neff, A. Prabhakar, S. Roosild

Tuesday, July 8

INTRODUCTORY SESSION - Chairperson: H. Ehrenreich

    Introductory Remarks by DARPA

    Overview of Field (T. C. McGill, MRC and CalTech)

GROWTH OF HETEROSTRUCTURES

    Theories of Growth, J. Singh (UM)

    Growth of III-V Strained-Layered Superlattices, R. Dawson (Sandia)

Chairperson: D. K. Ferry

    Growth of Si Based Microstructures, H. Markoc (UI)

    Growth of II-VI Superlattices, J. P. Faurie (Univ. Ill.-Chicago Circle)

    New Results on II-VI Superlattices, J. Schetzina (NLS)

    DISCUSSION

Wednesday, July 9

STRUCTURAL PROPERTIES OF HETEROSTRUCTURES - Chairperson: A. Prabhakar

    Theoretical Considerations of the Structural Properties of Heterostructures, J. Hirth (OSU and MRC)

    TEM Studies of Heterostructures, N. Otsuka (Purdue)

ELECTRONIC PROPERTIES OF HETEROJUNCTIONS

    Band Offset Measurements, D. Wolford (IBM)

    Electronic Properties of nipi's, P. Paul Ruden (Honeywell)

    Electronics and Optoelectronics Based on Si-Ge Heterostructures, O. J. Marsh (HRL)

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Chairperson: D. R. Osgood

Electronic Properties of Superlattices, D. L. Smith (Los Alamos)

Electronic and Optical Properties of Quantum Wires and Quantum Boxes, P. Petroff (ATT Bell Labs.)

DISCUSSION

Thursday, July 10

NOVEL APPLICATION OF HETEROSTRUCTURES
Chairperson: J. D. Murphy

Applications of Heterojunctions in Modern Electronic Devices, D. K. Ferry (ASU and MRC)

Detectors and Sources Based on III-V Superlattices, F. Capasso (Bell Labs)

Thin Layered and Lateral Microstructures, R. Nahory (Bellcore)

Applications of Superlattices as Nonlinear Optical Materials, A. Husain (Honeywell)

Chairperson: T. C. McGill

DISCUSSION

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ARMOR/ANTI-ARMOR

RELATIONSHIPS BETWEEN ARMOR PERFORMANCE AND MATERIAL PROPERTIES

A. G. Evans, B. Budiansky, J. W. Hutchinson and R. M. McMeeking

In complex processes such as the performance of armor impacted by a projectile, the development of associations between performance and material properties can only be effectively ascertained with the aid of numerical simulations, coupled with experimental measurements of material properties, as well as penetration tests and analysis. Such an approach has been utilized with moderate success for metallic armor having relatively low hardness, perforated by plastic deformation mechanisms. Associations between the penetration resistance and the dynamic plasticity characteristics of the armor (such as the Hugoniot elastic limit and the work hardening rate) have been elucidated. However, more advanced armors (such as ceramics and composites) have a penetration resistance dominated by damage processes in the materials: including cracking, shear banding and 'crushing'. The purpose of the present workshop was to ascertain the status of penetration resistance predictability (and relationships with material properties) for armor penetrated by damage mechanisms. Shear banding and cracking mechanisms of armor penetration were addressed, with emphasis on the role of numerical simulation and the influence of material properties.

SUMMARY OF RECOMMENDATIONS

Metal Armor

Conduct a study that strictly compares numerical simulations with experimental measurements and observations of the ballistic limit, determined for materials (steels) that exhibit transitions between plowing and plugging modes of penetration.

A successful study would provide the basis for meaningful numerical predictions of armor performance and trends in performance with material properties.

Ceramic Armor

Conduct a study that identifies the dominant mechanism whereby ceramic armor resists penetration. Such a study would entail large strain compression measurements on typical ceramic materials, subject to confining pressure, coupled with numerical simulations of penetration.

Once the prevalent mechanism has been identified, simpler tests could be initiated that compare a range of ceramics and ceramic composites with regard to their penetration resistance, thereby identifying the pertinent microstructural features that impart penetration resistance.

STATUS OF PRESENT CAPABILITY

Metallic Armor

High performance metallic armors frequently have a penetration resistance limited by shear bands, that cause plugging failure (Fig. 1). A review of present understanding of shear bands, and of code implementation, provided an encouraging sense of prospects for the predictability of shear band dominated penetration. The mechanics analysis of critical plastic strain levels for shear band formation, e_s has attained a sufficient sophistication that sensitivity studies are being conducted that provide a solid basis for both identifying the relevant material characteristics and the appropriate constitutive laws pertinent to code implementation. It is now possible to predict the general trends in e_s with such material properties as thermal conductivity, the temperature dependence of the yield strength, the work hardening coefficient, the strain-rate sensitivity and the kinematic hardening. Systematic experimental

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determination of these properties, for prospective metallic armor materials, would be insightful with regard to their relative merits in armor performance.
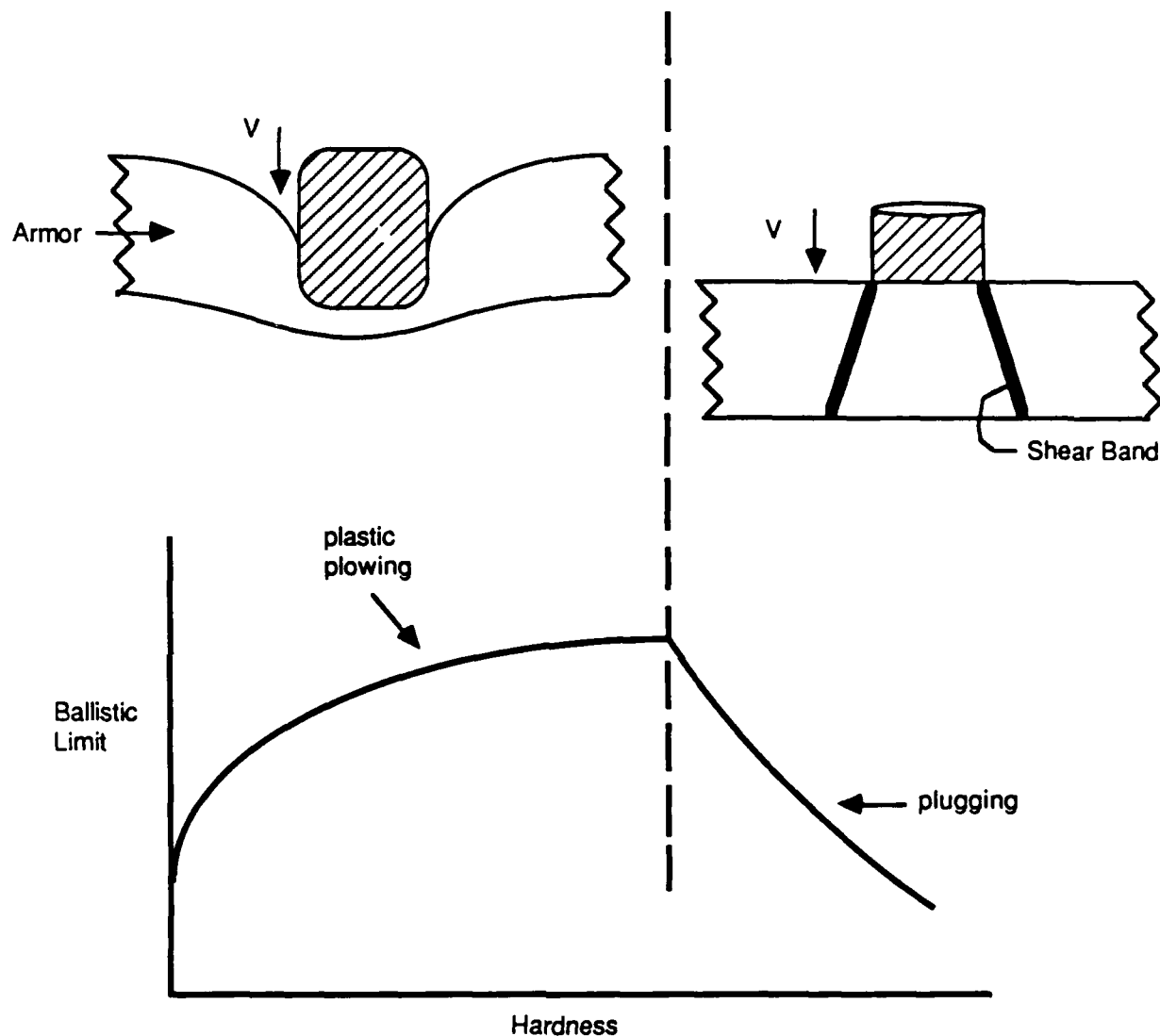
Figure 1. Transitions Between Plowing and Plugging Limited Ballistic Behavior of Steel Armors.

As they stand, the codes being used on penetration problems already incorporate some of the requisite constitutive features needed for predicting adiabatic shear banding but

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evidently not all. The most important missing ingredient is probably material strain-rate sensitivity, which is expected to play a decisive role in shear banding phenomena at the high strain-rates (10^3 to 10^5 s^{-1}) which characterize deformation in the bands. Foremost amongst the difficulties is the acquisition of high strain-rate properties associated with relevant temperature and strain histories. On the computational side, more experience is needed before it will be known how sensitive plugging failure predictions are to the size and distribution of the finite element grids. At the moment, no rules of thumb appear to be available to guide the code analyst in chosing the level of grid resolution necessary to adequately capture the shear band for his purposes. A carefully conceived study would determine whether these difficulties represent primary or secondary concerns and, hence, define the need for further fundamental understanding.

Ceramic Armor

The material properties that govern the performance of ceramic armor are not known, because the relevant deformation and damage mechanism that operate during the most critical phases of penetration have not been identified. Penetration studies pertinent to ceramics should thus be used to elucidate the dominant mechanism regimes for typical ceramic armors. Then, the potential for identifying the material properties that afford good penetration resistance would become possible.

Amongst the mechanisms involved in the penetration of ceramic armor are: plastic deformation (hardness), compressive failure (involving microcracking from heterogenities and subsequent shear faulting), flow of 'pre-crushed' material and tensile fragmentation. Each mechanism operates at various stages during penetration and in different locations within the armor. However, the dominant mechanism involved in resisting penetration is unknown. Some preliminary evidence suggests that, for ceramic armor encased in metal, the stresses in the ceramic can exceed the compressive strength, before the projectile penetrates to the ceramic. Should this be a typical

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condition upon penetration, clearly the constitutive properties of the 'pre-crushed' and constrained ceramic would dominate the penetration, i.e. the hardness and compressive strength of the ceramic would be irrelevant (to first order). In fact, consolidated ceramic powder encased in metal might then perform as well as a dense ceramic. Conversely, if the projectile is considerably retarded before compressive failure initiates, the compressive strength (and perhaps, hardness) of the ceramic would be the relevant material property. It is thus of paramount importance to ascertain the dominant mode of response, for typical impact conditions, before proceeding with other research. An approach needed to achieve these objectives, using a combination of mechanical testing and numerical simulation, is described below.

RESEARCH DIRECTIONS

Plugging

The ability to compute the impact conditions and material properties that dictate the onset of plugging-dominated penetration would provide considerable confidence in numerical approaches for both optimizing metallic armor systems and predicting the ballistic limit. A systematic study with this objective is thus advocated. John Mescall identified a system of steel armors that exhibit transitions from deformation to plugging-dominated penetration, with associated variations in ballistic limit (Fig. 1). Such behavior was deemed amenable to simulation, with the presently available mechanics of adiabatic shear banding.

The predictability of plugging undoubtedly requires some development of high-rate mechanical testing procedures and of the mechanics/numerics involved in shear band propagation (including the band width). However, the approach suggested would initially utilize available testing procedures/ mechanics/ numerics and ascertain the penetration predictability, based on high-strain-rate data (yield strength, work

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hardening, thermal softening, rate-sensitivity and kinematic hardening). Comparsion with penetration experiments would then determine deficiencies in testing and simulation that identify requirements for further development.

Details

Materials:

a.) Choose either an ESR on VAR 4340 steel, not the RIM steel. The reason is that RIM steels contain too high a density of inclusions (sulfides) which impart a complex phenomenology, involving premature micro-fracture. The first step should be to understand the failure process when essentially 'plasticity driven'.

b.) Choose 2 or 3 steels that have either different chemistries or have been heat treated differently to produce the same range of hardnesses. This is important in order to provide a sufficient correlation with material properties to begin answering questions about ideal properties.

c.) Perform penetration tests as a function of hardness and velocity, and perhaps temperature, and document the phenomenology of penetration thoroughly. This should include a microscopic study of damage or microfracture that may have occurred.

d.) Measure mechanical behavior at high strain rates (at least up to $10^4 s^{-1}$). Document yield and strain hardening and <u>strain rate sensitivity</u> as a function of temperature. Split 'Kolsky bars' have been developed to perform such measurements.

Constitutive Laws:

a.) 'Calibrate' appropriate large-strain versions of J_2-flow theory with the experimental measurements of constitutive properties. These laws must be both strain-rate and temperature dependent. This is important in order to understand the role of thermal softening and strain rate gradients.

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b.) If the experimental studies show that damage through void initiation occurs, it may be necessary to use a rate dependent 'Gurson' type model to account for porosity and the softening that results from damage by ductile 'micro-fracture'.

c.) Other constitutive models that include pressure dependence, or constitutive features such as the more complicated path dependent strain hardening found in kinematic hardening models, might also be used. Pressure dependence is, in any event, important.

Computations:

a.) Perform finite element calculations of the penetration problem. Computations should be carried out for problems directly comparable to experiments. Other calculations should be parameter studies to guide the design of armor materials.

b.) Computational procedures, including integration schemes and algorithms, as well as element choice and design, should be explained in detail along with time stepping methods and the error norms used to control accuracy.

c.) Special numerical procedures such as 'adaptive re-meshing' should be tested, and the results should be fully reported.

Strategy:

The calculations and experiments should be performed through a collaboration between groups at both DOD and DOE National Laboratory and University groups.

PENETRATION MECHANISMS IN CERAMICS

With such uncertainity regarding the prevalent penetration mechanisms in ceramics, a series of experiments and computations should be initiated that provide the requiste mechanistic knowledge. In this regard, it is noted that the penetration mechanisms are probably similar to those that obtain in other brittle solids, such as rocks

and concrete. Consequently, considerable insight could be gained immediately by transfer of the rocks/concrete body of knowlege into the ceramic armor arena.

Experiments

Tests that evaluate the compressive failure envelope for ceramic materials should be initiated. Initially, quasistatic measurements would be insightful, especially when a range of confining pressures are employed, and the crack initiating heterogeneties are identified by means of careful microscopic investigations. The failure envelope could then be correlated with micromechanics models, (analgous to that already developed by Nemat-Nasser for a pre-existing array of microcracks). Simultaneous determinations of the dilatation that accompanies non-linear deformation would also be necessary, as well as the characterization of strain levels that coincide with the onset of shear faulting. Furthermore, in some ceramic materials, brittle-to-ductile transitions could be anticipated (as in rocks) and, such transitions should be sought, characterized and correlated with micromechanics models.

Trends in compressive failure with strain-rate could be explored using experimental approaches outlined by Lankford, namely by means of Hopkinson bar and gas gun tests. Of particular interest would be the strain-rates at which the transition to 'transit-time' limited cracking occurs (Fig. 2), as well as the strain-rate dependence at higher strain-rates. Such results could then be superposed on the quasi-static measurements to provide generalized compressive failure envelopes pertinent to implementation in numerical simulations.

It is not sufficient, however, to confine experiments to the intitial failure envelope, because of the prospect that the ceramic is 'crushed' at an early stage in the penetration. Constitutive laws pertinent to the flow of constrained, pre-crushed ceramics are thus

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necessary. Again, quasi-static measurements of the compressive flow laws would be insightful and should be instituted.

Experimental determinations of compressive properties must be coupled with numerical simulations in order to ascertain the predominant mechanism of penetration resistance. The incorporation of a damage parameter into the numerical formulation appears to have merit as a description of some aspects of the compressive constitutive properties and should be explored. The initial objective of these simulations would be a determination of the sequence of material responses that accompany penetration of a typical ceramic subject to a typical impact. Such knowledge would provide a focus for further studies of ceramic properties pertinent to penetration resistance.

$$\sigma_c \sim \dot{\varepsilon}^{1/3}$$

Quasi-Static

COMPRESSIVE
STRENGTH
σ_c

Dynamic:

Transit-Time
Limited

Shear
faulting

| 10 | 10^2 | 10^3 | 10^4 | 10^5 |
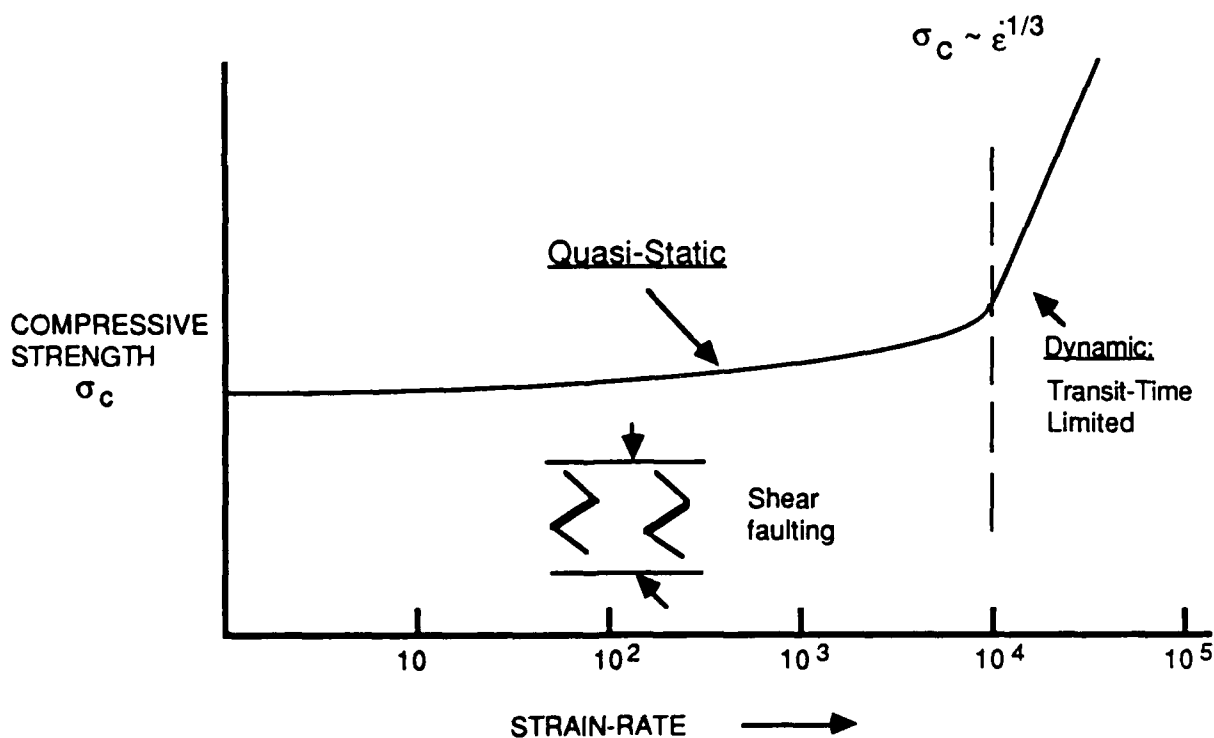
STRAIN-RATE $\longrightarrow$

Figure 2. Strain-Rate Dependence of Compressive Strength of Ceramics.

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AGENDA

ARMOR/ANTI-ARMOR
July 15-16, 1986

ARMOR: DYNAMIC FAILURE

Tuesday, July 15

INTRODUCTION, G. Farnum, A. G. Evans

The Phenomenology of Ballistic Impact, K. Frank, BRL

Incorporation of Fundamentals into Codes, J. Goudreau, LLNL

DYNAMIC FAILURE
Brittle Failure

Computations of Failure in Brittle Solids, J. Mescall, MTL

Mechanisms of Compressive Failure, S. Nemet-Nasser, UCSD

Compressive Failure of Ceramics, J. Lankford, SWRI

Fragmentation in Armor Systems, D. Shockey, SRI

Discussion (A. G. Evans)

Dynamic Brittle Failure: Status of Understanding and Incorporation into Codes

Wednesday, July 16

Shear Failure

Mechanics of Shear Instabilities, A. Needleman, Brown

Materials Aspects of Shear Bands, R. Asaro, Brown

Mechanics of Dynamic Ductile Fracture, M. Kanninen, SWRI

Discussion

Dynamic Shear Failure: Status of Understanding and Incorporation into Codes
(B. Budiansky, A. G. Evans)

Advances in Computational Methods Pertinent to Incorporation of Dynamic Failure Criteria
(T. Hughes, G. Hegemeier)

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INTERMETALLICS AND INTERMETALLIC COMPOSITES

R. Mehrabian, A. G. Evans, J. Williams, P. Parrish

INTRODUCTION

A two day workshop was held on processing, microstructure and properties of intermetallics and intermetallic matrix composites. Intermetallic materials offer a promising combination of high melting points, low densities and environmental stability. However, they are reactive in the liquid state, show low ductility (and strain rate sensitivity) at low temperatures and will have to be strengthened by precipitates, dispersions or particulates for very high temperature use. Rapid solidification processing and subsequent consolidation/deformation were emphasized as available techniques to broaden the phase diagram 'pathways' and hence available microstructures. The present understanding of properties of ordered intermetallics compounds were reviewed and their potential applications in advanced aircraft structures and gas turbine components were discussed. Fruitful discussions ensued regarding specific engineered microstructures for improved strength, ductility, toughness, high temperature creep, oxidation, etc.

RECOMMENDATIONS

Processing

Key issues in processing of intermetallic and intermetallic composites include:

- Thermodynamic analysis of stable and metastable phases should be conducted in systems of interest with special emphasis on calculation of T_o curves.

- Little is known about the solidification of intermetallic alloys. A comprehensive approach is needed to couple thermodynamic data with interface kinetic studies and transport phenomena modeling. This work should be closely coupled to controlled

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experiments with fine (less than 1 μm in size) and coarse (50 to 500μm in size) powders. Microstructure characterization should be closely coupled to the theoretical work.

- The overall processing work should be aimed at producing microstructures that have been designed by the micromechanisms researchers to meet specific property goals.

- There is a need to develop a better understanding of consolidation mechanisms of particulates produced through rapid solidification. Consolidation models need to be coupled to coarsening an phase transformations in order to preserve and/or produce desired microstructures.

Mechanical Property Optimization

- Obtain a comparison between theory and experiment regarding the effect on creep resistance of a bimodal distribution of particles, consisting of small equiaxial dispersoids and larger, rod-shaped reinforcements.

- Utilize the advanced understanding that exists in the reinforcement of brittle matrices by fibers, whiskers and ductile dispersions to predict toughening trends in brittle intermetallics. This would be achieved by conducting simulations of the sensitivity of toughness to the interface debond and sliding resistance and the matrix plastic flaw properties.

- Relate trends in the brittle-to-ductile transition to quantitative differences in the stresses needed for primary and secondary slip and to the microstructural features that control the cleavage strength. This study entails experimental measurements and analysis of flow stresses including consideration of the effect of ternary solutes in ordered lattices, observations of cleavage crack nucleation sites, as well as calculations of stress singularities associated with deformation heterogeneity at three/four grain junctions, martensite lathe edges, etc.

- Initiate a systematic study of the mechanisms of fatigue crack initiation and of

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crack growth thresholds in selected intermetallics. Such studies should include
consideration of short cracks.

- The compatibility between reinforcing phases and intermetallic matrices requires
systematic study. These studies should also consider the role of coatings on such
compatibility, and be coupled with the independent investigation of their role in
interfacial debonding and sliding.

SUMMARY OF PRESENTATIONS

Processing

Application of rapid solidification processing to production of stable and
metastable intermetallics, with or without second phase dispersoids, were emphasized.
The fundamental thermodynamic and kinetic aspects, such as metastable phase
diagrams and kinetic limitations, were first reviewed followed by examples of specific
microstructures/properties observed to date. The emerging consensus of the speakers
was that while novel microstructures/properties have been produced, the field is ripe for
fundamental advances and practical technological development.

The first presentation by John Perepezko covered both his, Mehrabian's and
Levi's preliminary studies in the field. He focused on the thermodynamic and kinetic
considerations necessary for prediction of phase selection sequences and relative
stability of the resulting microstructures. Many intermetallics form through peritectic
solidification with severe microsegregation. One important application of rapid
solidification is to suppress this segregation. A consideration of the thermodynamics,
nucleation kinetics and growth kinetics reveals some interesting phase selection
opportunities including alternate ordered and disordered phases with enhanced ductility.
Moreover, the structural constraints due to order signify that the growth kinetics of

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intermetallics is relatively sluggish so that alternate phase selection of ultrafine microstructures is quite possible.

Perepezko also described several examples of new results in promising alloy systems. In melt spun Nb-Si alloy deep undercooling and sluggish growth allowed for the development of multiple nucleation yielding an ultrafine grain size of 150Å. For powder studies a containerless processing drop-tube (at University of Wisconsin -Madison) and an electro-hydrodynamic (EHD) atomization apparatus (at University of California-Santa Barbara) have been developed to minimize reactivity and crucible contamination. The initial results from drop-tube experiments on Nb-Al alloys demonstrated that the brittle Nb_2Al, phase may be suppressed in undercooled powders by formation of a disordered BCC phase. The yield of metastable BCC phase is maximized for finer powder sizes. Other work on the TiAl intermetallic composition indicates that in fine powders (20-30μm) the Ti_3Al phase can form and can be decomposed into the equilibrium TiAl phase by annealing (800°C for 2 hr.). The yield of Ti_3Al in the powder was increased by changing from an argon to helium gas atmosphere in the drop-tube.

Perepezko concluded that the application of rapid solidification methods to the processing of intermetallics can contribute significantly to the development of unique microstructures and provide guidance in new alloy design.

A. Giamei summarized his work on NiAl and Ni_3Al systems. He noted that preliminary studies of microstructure - property relationships can be done on single crystals produced by Bridgeman or Float Zone crystal growth techniques. He reviewed a novel apparatus and technique developed at UTRC to produce splats of various reactive melts and obtain tensile data from same. Variation of the melt volume (and therefore splat thicknesses) can lead to cooling rates of 10^3 to 10^6 °K/s.

Giamei concluded that advanced composite systems will probably be required to toughen intermetallics; small pockets of ductile material or stiff reinforcement may be used to locally relieve strain or transfer load, respectively. Many choices are available including equiaxed platelet, whiskers and fiber reinforcements. Theory would appear to adequately predict stiffness and strength, but falls somewhat short in the area of creep resistance. Multi-modal dispersions and/or reinforcements may ultimately be required for the best balance of properties.

Specific examples of rapidly solidified composites with large volume fractions of submicroscopic (0.1 to 1.0 μm size) reinforcements in titanium alloys and intermetallics were given by S. Sastry. The reinforcements currently studied are rare-earth oxides, borides, carbides and nitrides. They are produced by rapid solidification and subsequent controlled decomposition of titanium alloys of the type Ti-Er, Ti-B, Ti-C, and Ti-N where Ti is any titanium alloy or intermetallic. The size and distributions of rare earth oxide dispersoids are such that Orowan type (dislocation bypass) strengthening is the dominant mode. In the case of boride and carbide dispersion strengthened alloys, strengthening arises from the "rule of mixture" type strengthening. Borides form 0.1 to 0.5 μm diameter, large aspect ratio (10:1) needles and rods. Carbides precipitate as spherical particles.

The thermal stability and strengthening produced by the reinforcements is currently being studied. Results thus far indicate that the alloys can be annealed at temperatures of 700 to 1000°C without excessive coarsening of the dispersoids. Strength increments of 25-100% of matrix strengths have been observed in the reinforced alloys at room and intermediate temperatures. However at 780°C strength increments decrease significantly. Fine grain size of these alloys was speculated to be the cause of low strength at high temperature. The need to produce larger second

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phase particles for improved high temperature properties were discussed in subsequent sessions.

Finally, R. Anderson discussed the practical aspects of producing rapid solidified powders of intermetallics by a crucibleless process. He described techniques developed at the Pratt and Whitney Government Products Division for production of small, several pound lots, to titanium intermetallic powders with and without rare-earth dispersoids.

Mechanical Phenomena

Aspects of the deformation and fracture of intermetallics and intermetallic composites were discussed, as well as some considerations pertinent to the oxidation resistance and hydrogen resistance of such materials. The principal objectives of the presentations were identification of materials and microstructures that provide a combination of good creep resistance and high toughness/ductility. Some basic features of dislocation motion in intermetallics and associated trends in ductility, fracture and fatigue were presented by Lipsitt. Lipsitt noted that to appreciate fully the effects of ordering on mechanical properties it is necessary also to understand the effects of ordering on crystal structure, slip systems, atomic bonding, and diffusion mechanisms. In addition, one must also consider the presence of thermal antiphase boundaries, the nature of grain boundaries in an ordered material, and the presence of constitutional vacancies in one or more of the ordered sublattices. These effects are most important and were reviewed by Lipsitt. He showed that the state of our understanding of atomic bonding, and the structure of grain boundaries in ordered materials is sadly lacking. Furthermore, the current state of our knowledge is insufficient to describe, even qualitatively, the role of the factors that determine the active slip systems, or the nature, the Peierls stress, and the mobility of the active dislocations.

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Lipsitt reviewed a wide range of mechanical properties, including hardness, elastic modulus, yield strength, work hardening, dislocation motion, ductility, ductile-brittle transitions, creep, fatigue, and fracture. He showed that most of the changes that occur in these properties upon ordering can be understood in light of the effects of ordering on the structure and physical properties. However, it become clear that ductile-brittle transition mechanisms seem to be independent of these physical property changes, and can only be discussed on a case by case basis. Lipsitt also noted that fatigue behavior is the mechanical property of ordered materials about which we understand the least.

The role of primary and secondary slip systems on ductility of intermetallic polycrystals was discussed by J. W. Hutchinson. He showed that triple points and vertices on grain boundaries induce strain singularities (even in fcc polycrystals with a single class of slip systems). In polycrystals of materials like many of the intermetallics which have two or more sets of systems with widely different flow stresses, the heterogeneous character of the deformation in the vicinity of triple points and vertices is even more accentuated. If the slip system hardens, then stress singularities occur along triple points and at vertices, albeit rather weak ones. These internal intensifications of stress and strain promote local fracture. The scale of these regions obviously scales with the grain size itself. Rather little is known about the stress and strain distributions at triple points or vertices even in simple systems with only one class of slip system. It seems like that the nucleation of fracture in intermetallics with primary and secondary systems of widely differing hardness will be strongly affected by the above-mentioned heterogeneity of deformation. A better understanding of the roles of the two classes of slip systems might shed considerable light on the fracture and ductility of these materials.

Prospects for toughening intermetallics were discussed by Budiansky. He showed that recent theoretical studies concerned with techniques for increasing the

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toughness of ceramics may provide prospects for analogous toughening of intermetallics. Embedding ductile metal particles in a brittle matrix can, under the right circumstances, enhance the fracture toughness of the unreinforced material, evidently by the mechanism of crack-bridging. (The classical examples is WC/Co--tungsten carbide containing cobalt inclusions; another system under study is Al_2O_3/Nb.) In this mechanism, intact particles join together the opposite faces of a crack, up to some distance behind the crack front, thereby impeding its advance. Necessary conditions for crack-bridging by particles are that the particle stiffness be less than that of the matrix, and that the particle-matrix bond be strong.

Fiber-reinforced ceramics, either with long aligned fibers, or randomly oriented whiskers, can be tougher than the basic ceramic, again with proper interface conditions met. Theory indicates that frictional slip between fiber and matrix plays an important part in this toughening process, with enhanced toughening results form lower slip resistance, however, leads to unacceptable matrix cracking in the presence of intact fibers. The predicted toughening (for the case of equal fiber and matrix stiffness) is:

$$K/K_m = \{1 + [s^3\, ac(1-c)/6K_m^2\, \tau\, (1-v^2)]\}^{1/2} \{1-c\}^{1/2}$$

where

s = fiber strength

c = fiber volume fraction

a = fiber radius

τ = interface frictional shear resistance

K_m = matrix toughness

K = composite toughness

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The stress-induced transformation of zirconia from tetragonal to monoclinic phase has been successfully exploited to toughen ceramics by the introduction of partially stabilized zirconia, the transformation of which at an advancing crack tip acts to inhibit crack growth. A similar toughening trick in intermetallics is conceivable.

The combination of transformation toughening and particulate toughening may be synergistic, with the increase in toughness more than the sum of the individual increases due to the separate effects. Again, the potential for synergism in intermetallics should not be overlooked.

Plasticity aspects involved in the toughening of intermetallics were described by R. M. McMeeking. He noted that the primary purpose of the reinforcements in intermetallic matrix composites will be to inhibit the growth of matrix cracks. However, this must be done without diminishing seriously creep resistance or creep failure properties of the material. To assess how this might be done, one must first consider the possible mechanisms of fracture of the intermetallic matrix by itself. The mechanisms suggested so far are cracking caused by grain boundary dislocation pile ups and stress intensification caused by plastic anisotropy of the flow of individual grains. Other mechanisms are possible, but it is likely that all of them can be phrased in terms of a critical stress or strain. In each case, a critical volume of material is necessary for the failure process to operate and this leads naturally to a critical crack tip opening displacement criterion for propagation of the matrix crack. Thus the purpose of the reinforcements in the composite structure will be to keep the crack tip opening below the critical level, or in other words, to shield the crack tip from strain.

In some cases, the reinforcement size and spacing will exceed greatly the size of a crack tip plastic zone which would otherwise be present in the matrix material. The effect of the reinforcements in protecting the crack tip from strain in this

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case of small scale yielding can be understood from the previous work on ceramic composites. The case which is in need of further modelling is that where the size and spacing of the reinforcements are comparable to or smaller than the matrix plastic zone. In this situation the interaction of the reinforcement and the plastic flow of the matrix must be accounted for. Consider the case of fiber reinforcement. This might induce void nucleation from the tips of the fiber, but any ductile crack propagation that results would require very large crack tip openings and so would be preceded by brittle matrix cracking. It is also likely that the crack would cut through the fiber unless it can be protected from such a failure. This could be done by fiber decohesion which would effectively blunt the matrix crack and relax the fiber stresses. Low interface strengths are desirable for decohesion to operate to the extent that flaws long enough to protect the fiber can be created. This is likely to place quite stringent limits on interface strengths compared to the ceramic matrix case. In addition matrix plastic deformation will distort the fiber, and it must be ensured that a fiber long enough and straight enough to strengthen the matrix by bridging the crack is left intact by this process. Model analysis of fiber decohesion in elastoplastic matrices is necessary to ensure progress on this problem.

Alternate mechanisms for protecting the fiber include the provision of a thin ductile coating. This will allow the crack to blunt by an amount inversely proportional to the yield stress of the layer. It must be ensured that a sufficiently low stress concentration in the fiber is achieved so that an intact reinforcement bridges the crack. The fiber will toughen the composite by bridging the crack. A Dugdale zone type of analysis can be carried out and the preliminary results indicate that long fibers would provide toughening increments comparable ceritus parabus to that produced in ceramic matrix composites.

Ductile phases in general offer some hope for toughness of composites. The bridging mechanism of particle toughening will only operate if the crack tracks to these inclusions. This will occur if the particles are plastically soft. The particles have the advantage that they do not provide an interconnected network for creep at high temperature. A skeletal network, on the other hand, should provide toughness by crack blunting mechanisms, but creep can operate in such a network. If the skeletal network is very thin, hydrostatic constraint stresses will build up in creep and thus strain rates for a given stress will be rather low. However, the same constraint can promote ductile rupture.

Transformation toughening is a promising mechanism, whether caused by dilating second phases or shear effects in martensites. In each case an extra increment of plasticity is present and this should help to inhibit crack propagation. If any significant dilation occurs, this is likely to provide closure stresses even through incompressible plastic zones and thus beneficial effects should occur as wakes of such material are created by growing cracks.

The oxidation resistance of intermetallics and intermetallic composites was described by F. S. Pettit. The oxidation resistance of some intermetallics was compared by examining the oxidation behavior of some Ti-Al, Ti-Cr, Ni-Nb-Al and Ni-Nb-Cr alloys under different experimental conditions. This comparison showed that the oxidation of intermetallics is consistent with the body of knowledge that exists for the oxidation of nickel and cobalt base superalloys and coatings on such alloys. In particular, oxidation resistance is determined by the characteristics of the reaction product scale that is formed upon the surfaces of intermetallics or intermetallic composites. Moreover, the more oxidation resistant systems are those that contain sufficient concentrations of elements such as Al, Si or Cr whereby continuous, external scales of Al_2O_3, SiO_2 or Cr_2O_3, respectively, are formed via a selective

oxidation process. While such oxide scales provide the most protection, other oxide scales such as NiO, TiO_2 or Nb_2O_5 can be used to provide protection when the oxidizing conditions are not too severe. While the oxidation behavior of an intermetallic is consistent with the existing data available for the oxidation of alloys in general, some intermetallics do possess certain characteristics which may create problems in using the selective oxidation process to develop adequate or good oxidation behavior. Some of these problems areas are:

1. The difference between the standard free energies of formation of the product phases is not large.

2. The solubility of oxygen in some intermetallics is relatively high.

3. The flux of the element to be selectively oxidized to the surface of the intermetallic may be low due to a small diffusion coefficient.

4. The growth rates of the oxides formed during the transient period may be high.

5. Some elements such as Ti may diffuse through protective barriers of Al_2O_3.

6. Other reactants in the gas phase such as nitrogen, carbon or sulfur may affect the selective oxidation process.

7. Some intermetallics are susceptible to "pesting."

8. There are data available that show that the mechanical properties of intermetallics can be very sensitive to the gas environment.

It may be possible to improve the oxidation behavior of certain intermetallics. Some modifications that should be considered are:

1. Add other elements to -

    • lower oxygen solubilities,

    • alter diffusion coefficients,

    • change crystal structure,

    • influence the effects of other reactants in the gas phase,

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- prevent pesting,

- decrease growth rates of oxides formed during the transient period.

2. Utilize microstructural control to -

- alter phase distributions,

- obtain homogeneous alloys,

- product oxide dispersions,

- optimize effects produced by grain boundaries on selective oxidation.

3. Use coatings or use techniques to modify the composition and structure of the surfaces of intermetallics.

The hydrogen resistance of intermetallics was described by Neil Paton. He noted that intermetallics such as nickel and titanium aluminides have the promise of low density combined with good high temperature strength. This combination of properties is of great interest for advanced hydrogen resistance of these materials - a logical step in their evaluation.

The expectation would be, that planar stiff materials, such as ordered intermetallics, could have a significant degradation in properties in high pressure hydrogen. This expectation is born out of a severe reduction in both strength and ductility of ordered $(FeNi)_3$, with the same alloy in the disordered condition only minimally effected by hydrogen charge. Ni_3Al in both high pressure hydrogen and electrolytic charging suffers significant degradation in mechanical properties. Experience with controlling and improving the hydrogen embrittlement resistance of nickel base superalloys, would indicate that improvements in properties of Ni_3Al type alloys might be achieved by microstructure modification. Slip dispersal by non-coherent particles might be one approach.

Hydrogen compatibility of TiAl and Ti_3Al alloys is largely unknown. However, the temperature at which Ti_3Al beings to dissolve hydrogen is considerably higher

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than α–Ti. TiAl on the other hand will not dissolve significant amounts of hydrogen even at temperatures up to 1000°C.

Nb Alloys Revisited

Wilcox noted that Niobium (Nb) is a metal with a very high melting point, 2470°C (4480°F), and a density comparable to nickel, ~8 g/cc; it thus offers the potential for greatly surpassing Ni-base superalloys (T_{mp} = 1450°C, 2660°F) in temperature capability for use in advanced gas turbine engines. It has been postulated that Nb alloys could have extended lifetimes under stress to 1480°C (~2700°F) in an oxidizing environment. It is known that Nb can be strengthened by solid solution alloying and precipitation hardening and can be alloyed to ensure non-catastrophic oxidation resistance. However, processing of these strong or oxidation resistant alloys by conventional methods (consumable arc or electron beam melting followed by forging or extrusion) is difficult because of ingot cracking induced by chemical segregation during solidification. Also alloying for oxidation resistance greatly lowers the melting point, and hence the creep resistance.

Questions raised by Wilcox included the following:

1. Using "new processing techniques, e.g., RST, MA, VADER, etc., "how" can Nb alloys be developed and processed for gas turbines (blades, vanes, flameholders, exhaust nozzles, etc.) which at a metal temperature of ~2700°F have:

- inherent (non-catastrophic) oxidation resistance?
- single crystal or elongated grain structure?
- sufficient creep strength (e.g., 0.1% strain in 1000 hr at 20-30 Ksi).

2. How can present coatings be modified or new coatings be developed to provide 1000 hr cyclic oxidation resistance in air at 2700°F?

3. If 1 and 2 can be accomplished, what are the payoffs?

- thrust-to-weight ratio?

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- turbine inlet temperature?
- uncooled components?
- cost?

SUMMARY OF WORKSHOPS AND DISCUSSIONS

Research Direction - Materials and Systems

For purposes of discussion, this session focused on two classes of materials:

Class 1. Monolithic intermetallic compounds (including conventional alloys, ordered phases, dispersion-strengthened phases) and particulate-reinforced intermetallic compounds.

Class 2. Continuous fiber-reinforced intermetallic compounds.

Discussion of Class 1 - Monolithic Intermetallic Alloys

The materials of this class have several features in common: They may be processed as bulk, isotropic materials, so that ingot or powder melt processing routes are available, as appropriate; they are conceptually amenable to deformation processing strategies (however, the process conditions, e.g., temperature, strain rate, etc., need to be highly controlled relative to that developed for ductile alloys); and, the overall balance of properties such as ductility, creep, fatigue resistance, etc., may be greatly affected by incorporation of dispersion, particles, rods, or platelets. In this part of the discussion, a major concern was expressed about the lack of single crystals of intermetallic compounds for investigation of slip/dislocation interactions, the relative role of (c) and (c+a) slip deformation, especially with respect to the effects of ternary additions to these compounds. Several investigators reported great difficulty in growth of single crystals with which to conduct such studies. One possible approach suggested was crystal growth onto a cold seed. The need to develop alternate (polycystalline) specimens for these studies was discussed, even

though the deformation studies would be conducted in a somewhat indirect manner. There was a discussion of the data in Fleisher's recent paper (J. Metals, Dec. 1985) which indicated that if one required high specific strength at high temperature, a series of berylide intermetallic compounds looked most attractive. Current binary phase diagram information indicates that these are line compounds; there is an urgent need to determine if appropriate ternary additions will broaden the phase field to some extent to make these compounds more producible.

Beyond the titanium and nickel aluminides, there was strong interest in intermetallics for niobium, e.g., Nb_3Al. There is a general need for selection criteria for intermetallics which have potential technological interest.

Discussion of Class 2 - Fiber Reinforced Intermetallic Composites

For intermetallic matrix fiber reinforced composites, several needs were expressed:

- There is a strong need for a broader range of fibers. SiC is not chemically compatible to matrices such as titanium aluminide, where TiB_2 or other fibers would be more appropriate if they were available. Alternatively, a strong need is for vapor phase or liquid coatings for reaction barriers between the fiber and matrix.

- New processing routes are needed beyond those currently utilized for melt infiltration processing of aluminum and magnesium matrix composites, such as Plasma, PVD or CVD processes.

- Proof-of-concept studies are needed to validate current micromechanics concepts for strengthening and toughening of fiber reinforced brittle matrix intermetallic systems such as TiAl. These studies should be further augmented by analytical and experimental efforts which address the micromechanics with the condition of a low ductility matrix where local plasticity effects may have a strong influence on properties.

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Mechanical Properties

The discussions focused on the influence of various types of dispersoids and reinforcements on the deformation and fracture properties of intermetallics, with the objective of identifying microstructures and materials that offer good creep resistance while having acceptable levels of toughness/ductility. The discussions emphasized creep resistance, toughness and the brittle-to-ductile transition.
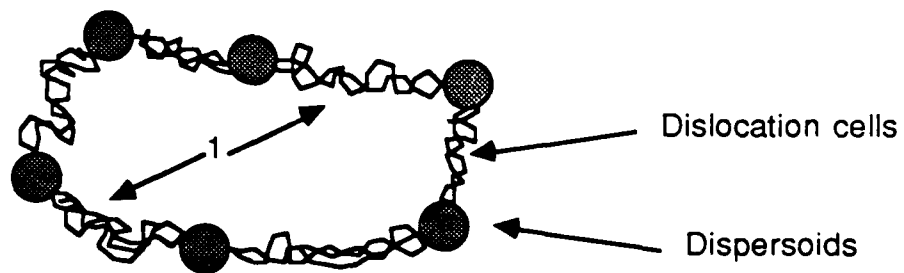
Creep Resistance

The deformation and creep properties can be modified by incorporating hard second phase particles at two size scales: small dispersoids that interact at the dislocation level and larger reinforcements that operate at the 'continuum' scale. The requirements at these extreme dimensional scales are very different. Dispersoids typically affect creep by reducing the dislocation cell size to a dimension comparable to the dispersoid spacing, l, resulting in a creep-rate having the form, $\varepsilon/D \sim [(\sigma - \sigma_0)/\mu]^8 (b/l)^3$ (Fig. 1), where σ_0 is a threshold stress, $\sim \mu b/3l$. A high volume fraction of small equiaxed dispersoids that remain stable at the operating temperature thus provides the best dislocation creep resistance. Such dispersoids also influence the flow stress such that, when incoherent but strongly adherent to the matrix, the hardening occurs is accordance with the Orowan mechanism, $\sigma \sim \mu b/l$.

Larger reinforcements that have dimensions appreciably larger than the dislocation cell also size have effects on both the creep resistance and the flow stress. Continuum analysis indicates a creep rate, $\varepsilon = A(c,s)(\sigma/\sigma_0)^n$, when n and σ_0 represent the creep coefficients of the matrix and A is a measure of the effect of reinforcement (with c being the volume fraction and s the shape of the reinforcement). Expected trends in A are depicted in Fig. 2 *. It is noted that rods and

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* (These expectations are based on calculations of shape effects for linear systems and of power law hardening trends for equiaxed particles.)

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'OLD' NOTION

Closely spaced, stable, 'hard' dispersoids

ADDITIONAL CONSIDERATIONS

Large reinforcement used to affect toughness, also to benefit

creep resistance

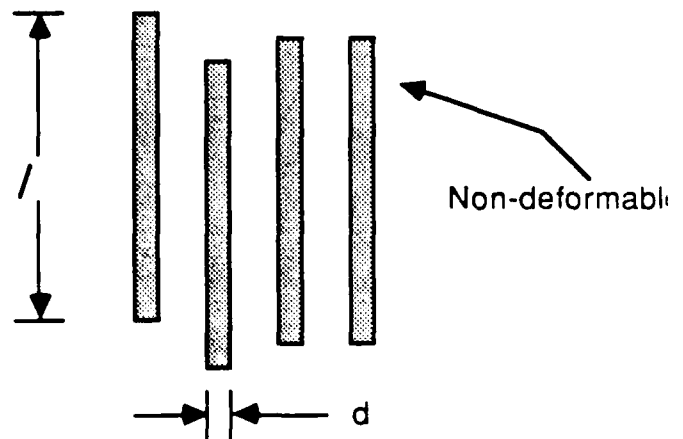factors:
- shape (l/d)
- volume fraction
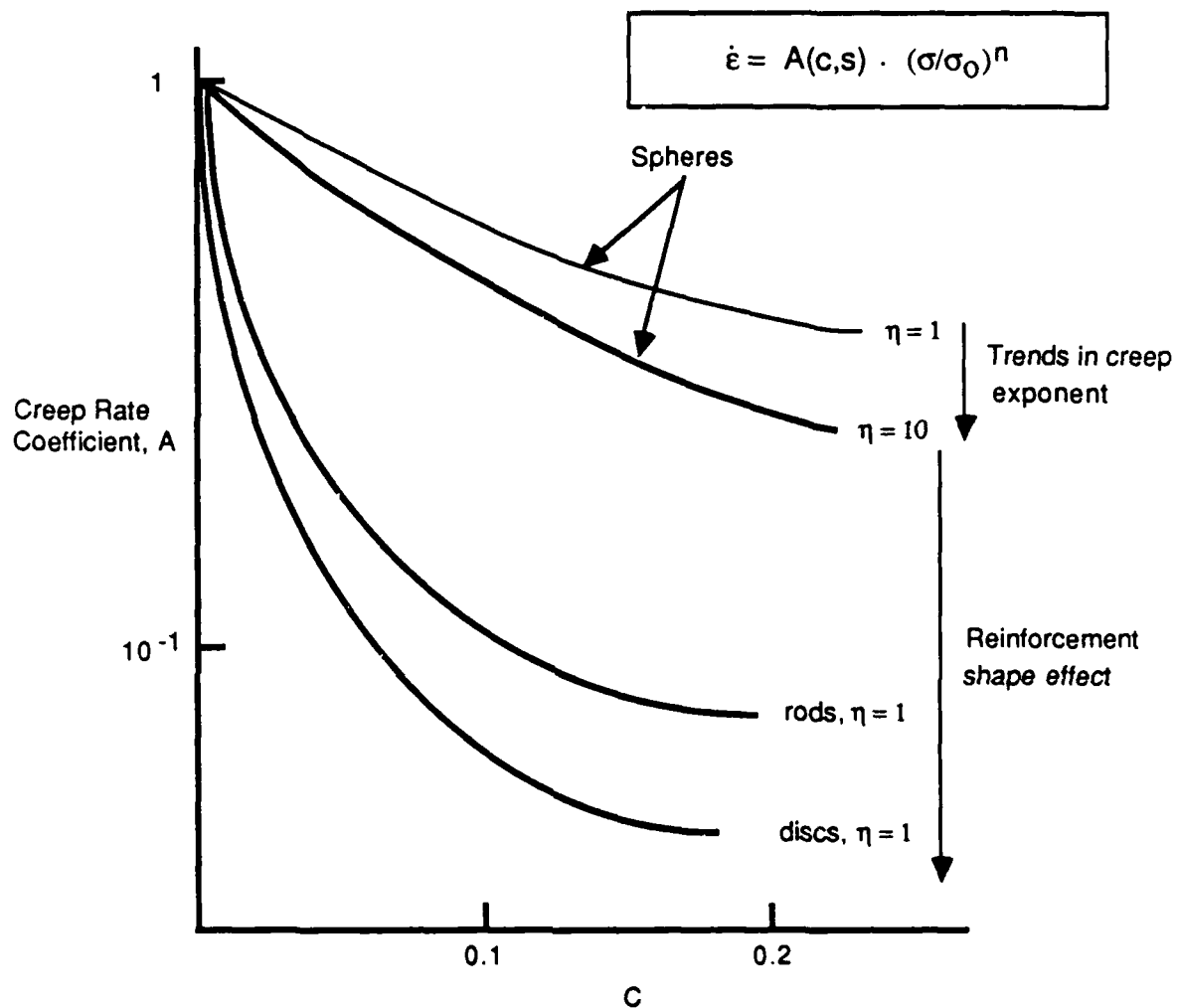

Figure 1. Creep Resistance

$$\dot{\varepsilon} = A(c,s) \cdot (\sigma/\sigma_0)^n$$

Figure 2. Effect of Reinforcement Shape on Creep Rate.

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discs are substantially more effective than spheres and that there is no effect of reinforcement size (or spacing), provided that the continuum size requirements are satisfied. It is also noted that A is a direct multiple of the matrix creep-rate. Thus, the maximum effect is achieved with a matrix that already has good creep resistance.

The preceding conclusion obtains provided that dislocation creep is the operative mechanism (Fig. 3). Should transitions to diffusional creep occur, when dispersoids or reinforcements are added, the creep resistance would not be appreciably improved by these additions. Then, larger grains would be needed to ensure enhanced creep resistance.

Fracture Toughness/Ductility

The effects on fracture of hard, elastic particles used to enhance creep resistance can be either detrimental or beneficial, depending upon the mode of matrix fracture: ductile or brittle (Fig. 4). The ductile fracture resistance is invariably reduced by the addition of hard (low ductility) particles, such that a systematic dependence on volume fraction obtains (Fig. 4). Furthermore, the fracture toughness exhibits a direct dependence on the hole nucleation strain, such that the particle size, shape and spacing become important. Specifically, holes tend to nucleate more readily at particles that are large, have a low interface debond resistance and have either angularity or a large aspect ratio. Such known characteristics allow decisions to be reached regarding the toughness degradation expected in metal matrix composites.

The brittle fracture resistance can be enhanced by the addition of brittle reinforcements, provided that local non-linear behavior can be induced at the reinforcement/matrix interface. Consequently, ceramic matrix composites have been made that exhibit a toughness which increases systematically with the addition of reinforcements (Fig. 4) and furthermore, have toughnesses that exceed the toughness of metal matrix systems having the equivalent reinforcement content. Interface

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non-linearity typically involves debonding, followed by frictional sliding.*
Calculations indicate that for such processes to occur, the debond toughness of the interface must be substantially less (by an order of magnitude in J) than the matrix toughness. With this proviso, the toughness increases systematically upon decreasing the shear resistance of the interface and increasing the fiber strength and radius (Fig. 4). Optimum ceramic matrix composites can thus be designed based on available micromechanics models.

For semi-brittle intermetallic matrices, the corresponding trends in toughness with the addition of reinforcements is presently unknown. Preliminary analysis of this problem (McMeeking) has suggested that the trend in toughness (upward or downward) is dictated by the magnitude of crack tip plastic zone, compared with the spacing between reinforcements. When the plastic zone is small, 'ceramic-like' behavior is most likely such that the toughness could be appreciably enhanced by the addition of reinforcements, subject to interfacial debonding or plastic sliding requirements. This occurs when $K_m \leq \sigma_0 \sqrt{12\pi R/c}$. When the plastic zone is larger, crack tip plasticity engulfs the fiber, causing fiber bending and premature fiber failure. Then, at best, only modest toughness enhancement would be possible. Such expectations clearly require systematic experimental and further theoretical investigation.

Ductile second phase regions invariably enhance toughness, when the region is intimately bonded to the matrix. Analyses by Budiansky and by McMeeking have revealed that the toughness has the following appropriate form: $K \approx 10\sigma_0\sqrt{R}[\sqrt{(1-c)}c(1-\sqrt{c})]$. Thus, toughening can be optimized by utilizing a dispersed phase having a high yield strength and large size with good ductility. The mechanism is clearly most effective when the matrix is brittle. However, poor bonding can cause the

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* (A thin ductile layer at the interface would offer the alternative possibility of plastic sliding, without debonding.)
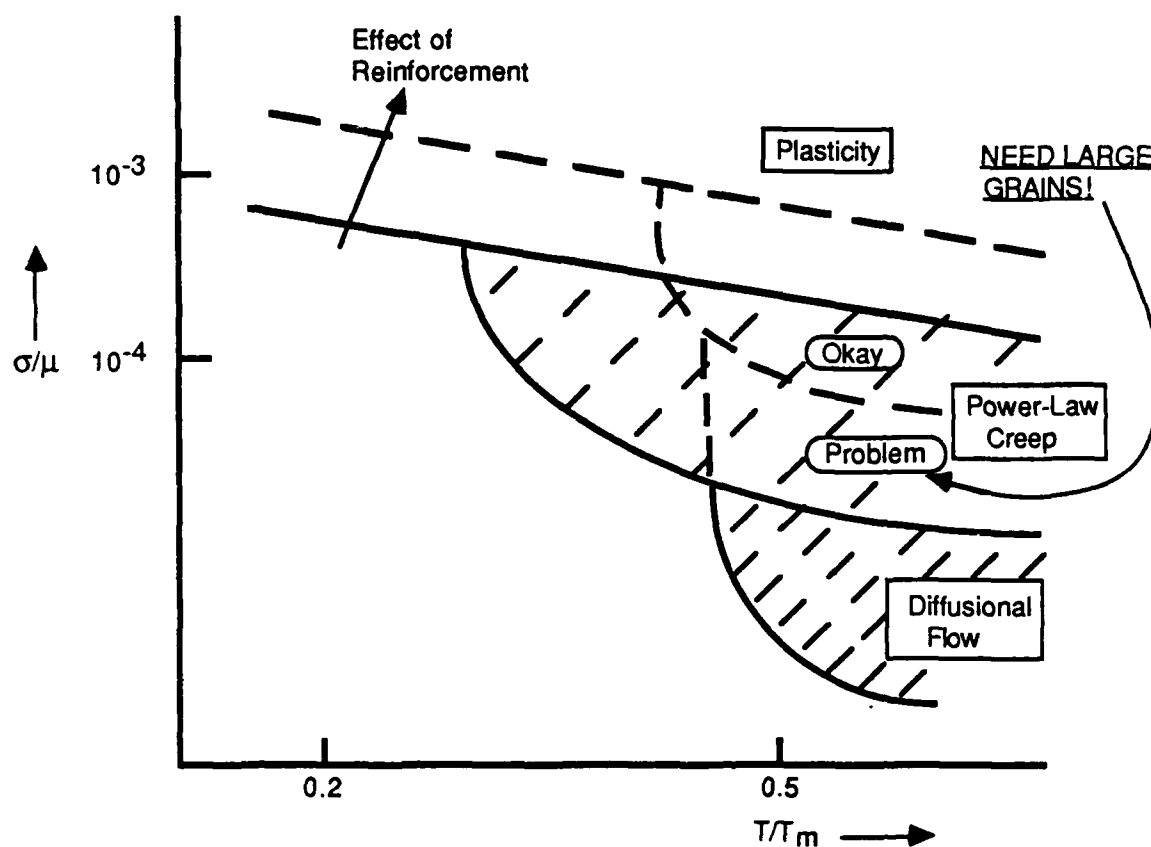
Figure 3. Deformation Mechanism Map.

Volume Fraction Reinforcement
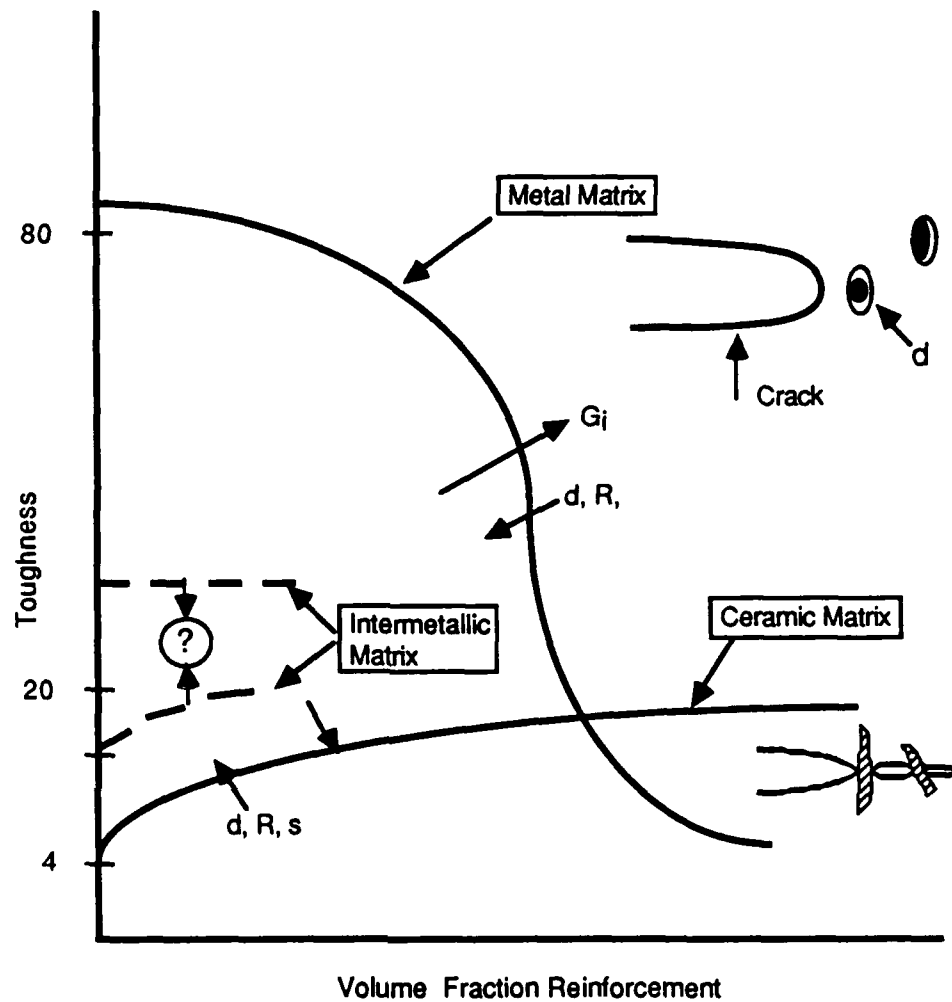
ISSUES:

Can relatively tough IMC composites be created?

- with toughness superior to best ceramic systems?
- also with good creep resistance?

Figure 4. Toughness of Composites

mechanism to become inoperative. A prerequisite for this mechanism is that the crack be attracted to the ductile phase. Present evidence suggests that this behavior obtains when the phase has a lower elastic modulus than the matrix. This toughening approach would appear ideally suited to intermetallics.

The Ductile-To-Brittle Transition

The induction of a transition from brittle to ductile fracture constitutes an alternative, well-explored, approach for improving the mechanical integrity. A <u>necessary</u> condition for polycrystalline ductility is that five independent slip systems operate. However, a <u>sufficient</u> condition for ductile fracture is that the maximum normal stress within the grain lie below the grain cleavage strength (Fig. 5). For polycrystals with differing flow stresses on the primary and secondary systems, relatively large normal stress tend to develop, especially near triple junctions (Hutchinson), that can exceed the cleavage condition (Fig. 5). Furthermore, cleavage has a characteristic microstructural length scale, which could be the size of hard particles in strengthened materials or the grain size in single phase materials. The appropriate microstructural dimensions for intermetallics have yet to be clearly identified. More understanding of the relevant dimensions would guide processing studies that have the objective of generating materials with enhanced toughness and ductility.
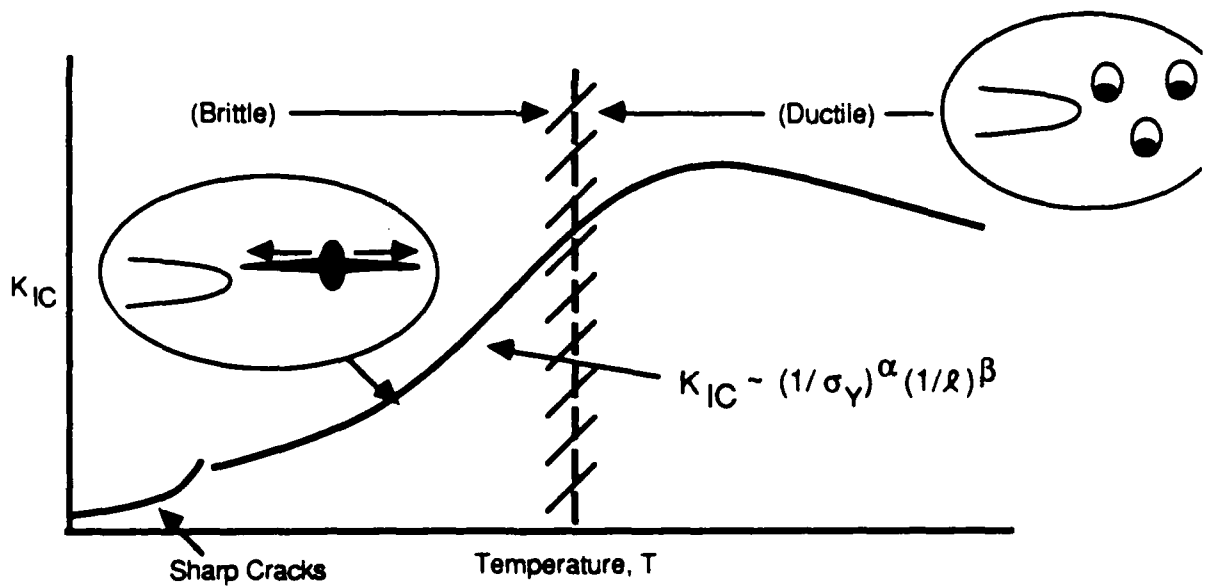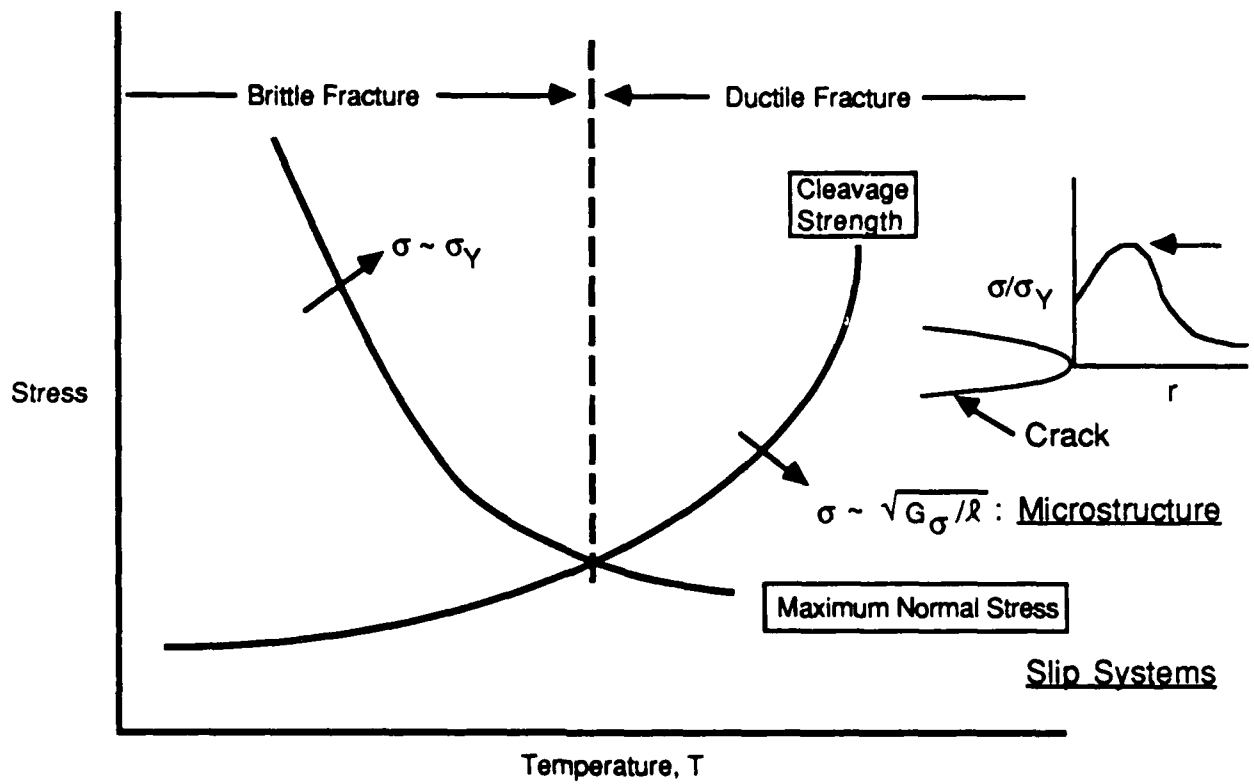
Figure 5. Trends Involved in the Ductile-To-Brittle Transition

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AGENDA

INTERMETALLICS AND INTERMETALLIC COMPOSITES

July 17-18, 1986
La Jolla, California

ORGANIZERS: R. Mehrabian, A. Evans, J. Williams, P. Parrish

Thursday, July 17

INTRODUCTION AND DARPA PROGRAMS/OBJECTIVES, P. Parrish, DARPA

INTERMETALLIC MATERIALS SYSTEMS AND APPLICATION, (P. Parrish)
M. Blackburn (United Technologies), A. Johnson (GE)

PROCESSING OF INTERMETALLICS AND INTERMETALLIC COMPOSITES BY
RAPID SOLIDIFICATION, (R. Mehrabian)

Thermodynamics and Kinetics, (J. Perepezko, Univ. Wis., R. Mehrabian, MRC)
Alloy and Composite System Selection Strategies (A. Giamei, R. Anderson (United
        Technologies), S. Sastry (McDonnell Douglas)

MECHANICAL PHENOMENA IN INTERMETALLICS AND COMPOSITES, (A. Evans)

Overview of Intermetallic Properties, H. Lipsitt (AFWAL)
Deformation Processing of Intermetallics and Composites, H. Gegel (AFWAL),
        P. Bridenbaugh (ALCOA)
Deformation and Creep of Reinforced Systems, J. Hutchinson (MRC),
        J. Williams (MRC)
Oxidation and Hydrogen Resistance, F. Pettit (U. Pitts), N. Paton (Rockwell)

Friday, July 18

PROSPECTS FOR INTERMETALLIC COMPOSITES, J. Hutchinson (MRC)

Interfaces, M. Ruhle (UCSB)
Toughness/Ductility, R. McMeeking (UCSB), B. Budiansky (MRC)
Titanium Aluminide/Silicon Carbide Intermetallic Composites, M. Herman (GM Allison)

NIOBIUM ALLOYS REVISITED, B. Wilcox (DARPA)

RESEARCH DIRECTIONS FOR REINFORCED INTERMETALLICS

Materials and Systems, R. Sprague (GE)
Processing, J. Moore (Pratt & Whitney)
Strength/Ductility, Toughness, J. Williams/A. Evans (MRC)

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SASTRY, S.	MCDONNELL DOUGLAS	314-233-2513
SIMNAD, M.	UCSD	
SINNOTT, M. J.	MRC/ U MICH.	313-764-4314
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WAX, S.	DARPA	202-694-1303
WHITESIDES, G.	HARVARD/MRC	617-495-9430
WILCOX, B.	DARPA	202-694-1303
WILLIAMS, J. C.	CARNEGIE MELLON/MRC	412-268-2477
YANG, L.	GA TECH.	619-455-2920

MAGNETISM AND MAGNETIC MATERIALS WORKSHOP

M. S. Dresselhaus, H. Ehrenreich and G. H. Vineyard

INTRODUCTION

A workshop on Magnetism and Magnetic Materials was held this year because of (1) the critical importance of this topic to the DoD, (2) the importance of this field to the national economy (representing a $20 x 10^9$/ yr. industry, of comparable size to the semiconductor industry), (3) new exciting research opportunities, (4) the decline of U.S. leadership in magnetics science and technology during the past 15 years, (5) the absence of a DARPA workshop on the subject in recent years.

At present, the leadership of the United States in magnetism and magnetic materials is declining rapidly, after two decades of U.S. domination of the field following World War II. The 1950's were a very active period for research on the fundamentals of magnetism in solid state physics, leading to the subsequent development of new magnetic materials, such as ferrites and garnets, amorphous magnetic alloys by rapid solidification (1967), magnetic bubble materials (1966), and rare earth permanent magnet materials (1966). The commercial development and exploitation of these materials dominated magnetic technology for the following twenty years. By the mid 1960's, support for research on magnetism and magnetic materials at U.S. universities declined, as other research fields attracted more attention. Research activity in the U.S. decreased in absolute terms, and shifted in emphasis, as the research effort moved to industry and became increasingly directed toward short term goals. By the mid 1970's, American manufacturers began to look increasingly to foreign sources for newer, better and cheaper magnetic materials and devices. In recent years it has become increasingly clear that the international role of the United States has been declining in the science of magnetic phenomena, in magnetic materials and in magnetics technology.

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Because of this decline and because of the importance of magnetic components for American industry and defense, the Department of Defense in January, 1984, asked the National Materials Advisory Board of the National Academy of Science--National Research Council to establish a Committee on Magnetic Materials. The committee was charged to assess the status of research and development in magnetic materials in the United States, to identify issues that may limit future development of magnetic materials and to recommend R&D areas with high potential for scientific and technological dividends. *The Report of the Committee on Magnetic Materials* (published in 1985) gives several arguments for strengthening the university research programs in magnetism and magnetic materials. Firstly, important new high leverage R&D opportunities are identified in areas which would significantly impact current magnetics technology with promise for future payoff, such as magnetic superlattices, magnetic phenomena at surfaces and interfaces and diluted magnetic semiconductors. Secondly the report emphasizes the need for a revival of a university research program on magnetism and magnetic materials with long term objectives. With a long term, high quality university research program in place, the stage is set for an effective coupling of the magnetics technology community largely in industry, to researchers in universities and National Laboratories working on fundamental and applied problems of long term significance. A third argument pertains to the needs of the industry and defense for highly skilled manpower in these fields; such personnel are reputed to be in especially short supply among young people.

The loss of U.S. leadership in theoretical magnetism studies is especially visible, as dominance was transferred to Japan and France. The loss of U.S. leadership in magnetics is in part related to the inferior U.S. facilities in the areas of neutron scattering (e.g., relative to the Institut Laue Langevin in France), pulsed and megagauss field research (e.g., relative to laboratories in Tokyo, Osaka and Sendai in Japan and in the

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U.S.S.R.). Whereas effective magnetics centers of critical mass and long term commitment to a broad range of basic studies and coupled device applications have evolved in Grenoble, Orsay, (France), and Sendai (Japan), no comparable institutions exist in the U.S.; the new centers at CMU and UCSD may in time broaden their scope and command comparable international attention. Also visible internationally is the rapid growth of the Japanese magnetics industry in the areas of magnetic components and new materials, leaving the U.S. industry far behind in the broad magnetics area. Though presently competitive in magnetic recording and amorphous magnetic metal tapes (Metglas) for transformer applications, U.S. industry is experiencing increasing competition from the Japanese, even in these areas of U.S. strength.

The national university magnetics program is particularly weak in basic science studies and in materials synthesis research. This is a general problem to be faced by the funding agencies broadly, not only by the DoE. In addition, there has been a demise in basic and applied advanced magnetics courses at universities, in tutorial review articles, as well as diminished coverage in basic solid state physics and materials science courses. Because of the interdisciplinary nature of magnetics technology, research programs of critical mass (e.g., Materials Research Groups in the NSF terminology) are of particular importance. To build a program which would adequately support industrial and defense needs and would keep the U.S. magnetics program competitive internationally, it is necessary to maintain a number of groups of critical mass in universities around the country, in addition to a few magnetics centers.

The DARPA workshop on Magnetism and Magnetic Materials held on July 21-22, 1986 provided a brief review of R&D needs and opportunities of DoD in this field. Despite the large size of the U.S. Magnetics Industry, the DoD requirements in state-of-the art performance are generally not being pursued by private industry. The major findings of the workshop are listed below. The complete program and list of

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participants is given in the Appendix.

IMPORTANCE TO THE DOD

Magnetism and Magnetic Materials are of strategic importance to the DoD in a number of vital areas. Almost every military weapon, device or vehicle depends on magnetic components in the form of motors, generators, transformers, actuators, transducers, sensors or speakers. Since many of these are airborne, the emphasis must be on high performance, lightweight magnets, exploiting the order of magnitude improvement in performance/weight achieved in the past decade, with promise for significant further achievements in the future. High sensitivity magnetic field sensors are clearly needed for identification, detection and monitoring applications, requiring increasingly sensitive magnetomechanical capabilities, exploiting the higher magnetostriction and magnetic anisotropy provided by advanced magnetic materials. In the high frequency electronics area, present requirements call for increasing the operating frequency of systems and devices (radar, communications links, signal processing) from the 1 to 35 GHz regime up to the 65 to 95 GHz regime. Components of interest include non-reciprocal isolators, rotators, modulators, spectrum analyzers, convolvers and correlators, deflectors, switches, tunable filters. Corresponding components are needed for future optical communication systems with promise for much higher data rate transmission and storage.

With regard to the 65 to 95 GHz (millimeter wave) regime, the frequency response of ferrites fails, because their natural resonance frequencies are too low. The resonance frequencies are determined by the product of M (magnetization) and H_a (anisotropy field). While M for insulators is limited to the 2 to 4 kG range, metals can give an order of magnitude increase in M, and new permanent magnet alloys can give several orders of magnitude increase in Ha. It has previously been assumed that the

limiting factor in using magnetic metals at microwave frequencies is the large ferromagnetic resonance linewidth. It has recently been demonstrated that by using thin, high-quality single-crystal magnetic metal films, ferromagnetic resonances at 35 GHz can be achieved with line widths comparable to those traditionally achieved with ferrites.

The increased frequency of communications systems is strongly coupled with the need by the DoD for high data rates and non-volatile memories for information storage and retrieval. The areas of greatest current interest include magnetic recording, magnetic-optical recording and vertical Bloch line memory (see Section on High Speed Data Storage). Though rapid advances in magnetic and magneto-optical recording are currently being made in industrial laboratories, there is only a sub-critical industrial commitment to the fundamental, long-term research that will affect developments in the field a decade hence. For this reason, DoD funding is needed to meet the high DoD performance requirements. If adequately supported, the two new centers at Carnegie Mellon University (Magnetic Technology Center) and at the University of California, San Diego (Center for Magnetic Recording Research) should go a long way in meeting DoD needs in a number of important focused areas. In addition, a magnetics center emphasizing high magnetic field phenomena could be established at the Francis Bitter National Magnet Laboratory, by strengthening their present program and exploiting their unique high magnetic field capabilities.

UNIQUE TECHNOLOGICAL OPPORTUNITIES

Many technological opportunities were identified at the DARPA Workshop. In the discussions that followed, three manor areas for DARPA support and attention were identified: New Magnetic Materials, Magnetic Control of Semi-conductor Dev... High Data Rate Storage and Retrieval. We elaborate below on these te... opportunities, followed by the basic research that must be done to ...

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is followed by a brief summary of characterization tools that must simultaneously be developed to carry out both the research and development work discussed above.

New Magnetic Materials

A variety of advances in solid state physics, high vacuum technology, computer control and materials processing capabilities have led to unique opportunities in the synthesis of new magnetic materials. It is generally felt that new magnetic materials with specially tailored properties, with extremes in properties (anisotropy, coercivity, magnetostriction, etc.) or with specially designed patterning or shapes will be the driving force for future technological magnetics applications. It is for this reason that we recommend that particular emphasis be given to strengthening the U.S. magnetic materials program in a major way.

The newest and most unusual magnetic materials are the magnetic multilayers and superlattices. By using molecular beam epitaxy, it is possible to prepare magnetic heterostructures with layer by layer control of the deposition, in analogy with semiconductor heterostructure superlattices (e.g., $GaAs/Al_xGa_{1-x}As$), which have been extensively studied for the past decade and now are beginning to find unique device applications. A large variety of magnetic multilayers should be possible, including two similar magnetic species, such as ferromagnetic Fe and Ni; two dissimilar magnetic species such as anti-ferromagnetic Cr and ferromagnetic Ni; a magnetic metal and a non-magnetic insulator; a magnetic metal and a non-magnetic semiconductor or insulator, a magnetic metal and a superconductor, etc. It is expected that these magnetic multilayers will have interesting and unusual properties, which can be exploited in device applications.

In the case of epitaxial growth of metals on substrates, interesting new interface structures have been observed between dissimilar crystal structures. For example, because of lattice constant compatibility, it is possible to grow thin (110) films of BCC

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Fe(a_0 = 2.866Å) on a (110) GaAs face $a_0/2$ = 2.827Å). It is thus expected that superlattice growth of Fe/GaAs layers can be achieved in a strained layer superlattice configuration. Although the study of magnetic metal/semiconductor interfaces is still in its infancy, a remarkable narrow ferromagnetic resonance linewidth has been demonstrated in Fe/GaAs at 9 GHz, showing promise for eventual application to millimeter wave radar components where ferrite materials show a degradation in performance. As another example, it has been demonstrated that it is possible to grow metastable metallic crystal phases by epitaxial multilayer growth; Zr grows epitaxially with a metastable BCC structure on a BCC Nb substrate, in contrast to the hexagonal structure found in bulk Zr. The extension of this principle to the epitaxial growth of magnetic films could lead to metastable magnetic phases with interesting and unusual properties.

Another exciting approach to new magnetic materials synthesis can be described as theory-assisted engineering of multicomponent magnetic alloys with either stable or metastable structures for special end use properties or for the demonstration of extremes in properties, such as magnetostriction, coercivity, anisotropy, magnetoresistance, magneto-optic effects, magneto-elastic coupling, Curie temperature, magnetization, temperature dependent properties, Faraday rotation, etc. According to this approach, each of the constituents of the multicomponent alloys is selected for some special set of properties, and then combined with other constituents in concentrations selected to optimize certain desired properties. Long term commitment to this approach has been amply rewarded in the past. For example, dramatic improvements in permanent magnet materials have been achieved for the past 30 years by this approach, with the synthesis of SmCo alloys in the 1970's, and the $Nd_2Fe_{14}B$ alloys in the 1980's, providing a substantial increase in the BH product over predecessor materials. It is believed that significant improvements in the BH product can be achieved by this approach. Attractive

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possibilities also exist for the development of advanced materials optimized for other applications. What is particularly lacking in this country is a viable university-based program in new multicomponent magnetic materials synthesis. An investment in such a synthesis program at a university with a strong experimental and theoretical magnetics program should have a high payoff.

Of particular interest to the DoD would be the development of better magnetic materials for low observable applications. Magnetic substances can be used in special coatings that have low reflectivity for radar. Ferromagnetic powders with high permeability, from which a composite is made, are particularly suitable. It is useful to be able to tailor the dependence of the permeability on frequency, and it is probable that there are unexplored opportunities for improvements of this kind. There is also a serious need for materials that retain high permeability to higher temperatures, which implies higher Curie temperatures.

This is but a very small sample of interesting and important magnetic materials synthesis opportunities. We believe that significant potential remains in the exploitation of rapid solidification technology to make amorphous low loss magnetic tapes, of ion implantation to prepare patterned buried magnetic films with controlled depth profiles, and of sputtering technologies for the preparation of granular magnetic particles. Long-term commitments will be needed to optimize the materials for specific device applications.

Integrated Magnetic Control of Semiconductor Devices

A second important area of technological opportunity is the newly emerging possibility of integrating magnetic elements into planar semiconductor electronics. Because of their lack of time reversal symmetry, magnetic elements are non-reciprocal, thereby making possible a host of directional properties, which can be exploited in applications such as rotators, phase shifters, isolators, switches, tunable filters, etc.

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Preliminary work has demonstrated the feasibility of growing magnetic films monolithically on semiconductors to exploit the unique device capabilities of both classes of materials for integrated circuit applications.

Of particular interest to the DoD is the development of high frequency circuit elements for microwave and millimeter wave technology. Several hybrid semiconductor/magnetic film device concepts have been formulated and were presented at the DARPA workshop.

The first device concept is a magnetically controlled high frequency delay line using a strip-line geometry where a magnetic Fe film forms a strip-line guide over an insulating GaAs dielectric waveguide. By rotation of the magnetization of the film relative to the microwave H field, the effective permeability is varied, and hence the propagation velocity of the wave can be controlled. Thus the device provides a smoothly adjustable high frequency delay line by controlling the direction of magnetization of the Fe film.

If the magnetic film is now operated near its resonance frequency $v_0 = \gamma\sqrt{H(H+4\pi M)}$, it will couple strongly to the waveguide near resonance v_0 when the magnetization M is along the propagation direction, causing power absorption near v_0. Tunability of this notched filter is provided by the magnitude of the small externally applied field H.

If the dielectric waveguide is channeled between two magnetic films which are magnetized transversely to the channel, a non-reciprocal strip-line isolator can be made. By introducing a doping gradient normal to the planes of the device, the electromagnetic wave in the dielectric waveguide is deflected when the magnetization is normal to the electromagnetic H field and to the propagation directions. Non-reciprocal loss is achieved for propagation in the two waveguide directions, so that the device has the properties of an isolator.

Magnetic Fe films could also be incorporated into monolithically integrated

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circuits based on diluted magnetic semiconductors, such as $Zn_{1-x}Mn_xSe$ to provide magnetic fields at low power inputs to drive the magnetic c=semiconductor material. The large field from the Fe films ($4\pi M \simeq 20,000$ Oe) could then be manipulated by small externally applied magnetic fields.

The development of monolithic hybrid semiconductor/magnetic film integrated circuits offers great promise for applications to microwave and millimeter wave systems. It is highly recommended that some critical mass university-based effort be initiated in this topical area, involving professors with expertise in both magnetic and semiconductor devices and fabrication. Coupling to an existing magnetism and magnetic materials program would be desirable.

High Speed Data Storage and Retrieval

The DARPA workshop identified High Speed Data Storage and Retrieval as a third area of technological opportunity for the DoD, with subtopic headings of Magnetic Recording, Magneto-optics, and Bloch line Memories. This area of opportunity differs from the other two in several ways. There is already a large R&D effort (which is more D than R) in magnetic recording in U.S. industry. In addition, there are two newly established University Centers at CMU and UCSD with focused research programs in this area. In this context, a proper role for the DoD is to selectively fund research of particular relevance to DoD needs, and to support basic studies necessary to further the field, but which will not be supported by industry.

A number of generic problems in magnetic recording were identified in the workshop. Micromagnetics studies are needed to delineate the pertinent magnetization reversal mechanisms and their dependence on particle size, field direction, field non-uniformity, and surface doping. Since the interaction between magnetic particles in the recording medium are long range, study of these interactions is vital for the understanding of the recording process, especially vector hysteresis phenomena. Good

two and three dimensional microscopic and macroscopic signal theory models are required to optimize both longitudinal and perpendicular recording media and to choose between them for specific applications. Noise and interference studies are needed to better understand the contribution from pair correlations between magnetic particles and from the transition regions to determine non-linear bit-shift limits on the error rate or the ultimate limit on the transition density. Study of the archival stability of the medium requires understanding of the superparamagnetism of interacting arrays. Fundamental studies of recording head fields are needed to gain understanding of 3D effects, saturation phenomena, and high frequency losses.

Magneto-optic recording represents a frontier area of opportunity for high speed storage and retrieval because of the ultra-high density of the information storage ($\sim 10^8$ bits/cm^2). This technology is especially attractive for the operation of very high frequency devices. To implement the technology, optical signal and data processing will be required and the devices themselves will be based on monolithically integrated optical and semiconducting components. A major effort on new thin film materials will be needed, including hybrid magnetic and semiconductor heterostructures and non-equilibrium materials prepared by advanced growth techniques such as magnetron sputtering and molecular beam expitaxy. A more fundamental understanding will be needed of magneto-optic phenomena in both single crystal and amorphous magnetic materials, including an understanding of the origin of magnetic anisotropy in an amorphous magnetic material.

The Vertical Bloch Line Memory is another emerging technology with great promise for high density storage ($\sim 10^9$ bits/cm^2) and with especially attractive prospects for rapid content-addressable search hardware. This memory, based on magnetic bubble technology, uses the internal structure of the domain wall for information storage, where the information bit is 0 or 1, depending on the presence or absence of a Bloch line

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pair in the wall. The absence of moving parts makes this technology particularly attractive for specific applications, offering promise for high reliability under extreme environmental conditions. Since the Vertical Bloch line memory is based on magnetic bubble technology, there is virtually no involvement by U.S. industry in these developments; they are however being pursued vigorously in Japan. The research issues that need to be addressed include the stability and dynamics of Bloch lines, materials design and optimization, the development of fabrication techniques, and device designs based on the Vertical Bloch line technology.

University involvement in each of the three above mentioned areas of magnetic recording science and technology is needed, especially for fundamental studies not supported by industry. University involvement is also necessary to train the next generation of innovative investigators, needed by industry and for national security.

IMPLIED SCIENTIFIC NEEDS AND OPPORTUNITIES

Significant advances in our fundamental understanding of magnetic phenomena will be needed to implement these technological opportunities. Since many of the same fundamental issues affect progress in the various technological areas, it is appropriate to treat the implied scientific needs and opportunities collectively. Better theoretical understanding is needed of such fundamental issues as magnetic anisotropy, magneto-striction, coercivity, magneto-optic phenomena, loss mechanisms, ferromagnetic linewidths in metals, magnetoresistance, Hall effect, magnetic viscosity and magnetic fluctuations. Better understanding of phase formation and phase transitions should help to predict new materials' phases and to search for new rare earth-transition metal multicomponent compounds for specific applications. Electronic structure calculations can now be done on complex multicomponent systems. Through a more fundamental understanding of the electronic structure of these materials, it may be possible to predict

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new materials combinations with perhaps superior properties.

Study of magnetic interactions between particles and clusters should lead to advances in magnetic recording media. Understanding the fundamental limits of magnetic parameters should be helpful in optimizing magnetic materials for special performance requirements. Better understanding of the fundamental properties of amorphous and microcrystalline magnetic materials, including their magnetic anisotropy is needed to tailor their magnetic properties, by control of their microstructure. To match the sophistication of the epitaxial growth of semiconductor heterostructures, extensive progress is needed in both the physics and materials science of epitaxial growth of metals, including dissimilar metal interfaces, metal/metal or metal/semiconductor interfaces with different crystal structures but with good lattice matching (e.g., Fe on GaAs). Similar studies will be needed for gaining an understanding of the magnetic insulator/semiconductor interfaces. Such studies could have a significant impact on optical and microwave signal processing, and semiconductor data processing using magnetic storage. In this work, attention to the nature of the interface composition, microstructure and surface states will be of particular importance. One especially promising interface is that arising in magnetoelectric multilayer structures, employing both piezoelectricity and magnetostriction to provide coupling between the electric and magnetic polarization phenomena in each of the constituent layers.

To make extensive progress with the integrated magnetic control of semiconductor devices, a deeper understanding of the coupling across magnetic and semiconducting interfaces will be needed. In addition, the foundations for device physics and modeling of integrated circuits with non-reciprocal magnetic components will have to be developed.

There also exists a whole class of unique new scientific opportunities in the field of magnetism and magnetic materials, unrelated to presently identified technological

opportunities. The possibility of synthesizing a wide variety of different kinds of multilayer and superlattice structures based on magnetic materials opens up a great wealth of scientific opportunity, now ripe for investigation. Related to the magnetic superlattices are the magnetic intercalation compounds which permit the synthesis of periodic structures with magnetic monolayers having atomically abrupt interfaces. The staging phenomenon permits separation of the magnetic layers by large distances, thereby making possible studies of 2D magnetism. Closely related are the magnetic monolayers that can be prepared on clean surfaces, permitting study of a variety of magnetic surface phenomena. The magnetic properties of various combinations of metal-metal, metal-semiconductor, metal-insulator, overlayers, sandwiches and superlattices have been simulated, exploiting the enormous power of presently available supercomputers. This power is growing rapidly, allowing even more complex problems to be tackled in the near future. Predictions to date have been dramatic, and some experimental verification has already been realized. Improved calculations including magnetic anisotropy and finite temperature effects should have significant impact on future higher resolution experiments.

The recent discovery of icosahedral symmetry in rapidly solidified magnetic materials suggests a search for novel magnetic properties that may be associated with this novel quasi-crystal structure.

ADVANCED CHARACTERIZATION

New sensitive characterization techniques for magnetic materials are now becoming available, permitting structure/property analysis on a microscopic level. Many of the most powerful techniques involve polarized electron spectroscopies, where the polarized electrons interact with the magnetic spins. The two techniques which have thus far had the greatest impact are scanning electron microscopy polarization analysis

(SEMPA) and polarized Auger spectroscopy. SEMPA is a highly versatile technique, sensitive to 100Å features in magnetic microstructure, having been successfully applied to such technologically important materials as magnetic recording materials and hard $Nd_2Fe_{14}B$ ferromagnets. Polarized Auger spectroscopy has likewise been used extensively to provide unique compositional information of magnetic domains. A number of other polarized electron spectroscopy too's for special applications are now available or under development. Examples of polarized electron spectroscopy tools include elastic electron scattering (LEED) with polarized electrons, inelastic electron scattering (EELS, the polarization aspects of which are still under development), polarized UV photoemission or inverse photoemission, polarized electron capture spectroscopy. XPS photoemission with polarized electron detection capabilities is still under development. One of th most informative electron beam instruments for the study of magnetic microstructure is the transmission electron microscope, operating in the Lorentz *configuration.* Conversion electron Mossbauer spectroscopy has also been shown to provide valuable magnetic depth profile information in the 0 - 1500Å range with a resolution approaching 50Å.

Neutron scattering has been a dominant long term tool for the study of magnetic phenomena, utilizing th interaction of magnetic spins in the sample with the magnetic moment of the neutron probe. Of particular importance has been the high sensitivity of the polarized neutron scattering instruments. Because of the outstanding quality of the U.S. neutron scattering groups, they have managed to maintain a competitive position in this field, despite the much larger, better instrumented groups abroad (e.g., at the Institute Laue Langevin). Revitalization of the U.S. effort is needed to maintain a competitive position as many of the U.S. principal investigators reach retirement age. As the capabilities of the pulsed neutron sources in the U.S. are enhanced, new research opportunities will become available. Also significant in this connection is the recent

development of sufficient sensitivity using synchrotron irradiation sources and sophisticated instrumentation to study the small but important effects associated with inelastic x-ray scattering by magnetic spins.

The magneto-optics techniques (e.g., based on the Kerr and Faraday effects) provide valuable characterization tools for study of the spatial magnetization distribution, and are also used for reading bits in magneto-optic disc memories. Since the interactions between magnetic spins and photons is very weak, high intensity synchrotron radiation sources are needed for the observation of magnetic x-ray scattering; such effects have recently been observed. There is promise that a polarized scanning tunneling microscope may soon be constructed, providing unique information on surface magnetism, surface domain nucleation phenomena and magnetic vortices.

The best magnetic characterization facilities in the U.S. have developed in national laboratories. Little high resolution magnetic characterization equipment is commercially available.

SUMMARY

In view of the great importance of magnetic components and magnetic technology to DoD operations, increased relative funding for magnetics R&D is strongly recommended as a highly cost-effective strategy for DARPA. Three areas of special opportunity and high priority were identified in the DARPA Workshop: New Magnetic Materials, Integrated Magnetic Control of Semiconductor Devices, High Speed Data Storage and Retrieval.

With regard to new magnetic materials, high priority should be given to the synthesis of novel magnetic multilayer and superlattice structures and the development of unique devices based on these structures. High priority should also be given to theory-assisted engineering of multicomponent magnetic alloys for special end-use

applications such as maximum B-H product, largest magnetostriction, highest magnetic anisotropy, etc.

Integrated Magnetic Control of Semiconductor Devices may be achieved by exploiting the coupling of epitaxial thin magnetic films to semiconducting substrates. Priority should be given to developing processing technology for the controlled fabrication of thin magnetic structures on semiconducting substrates and for the development of unique magnetically controlled device structures with particular relevance to millimeter wave applications.

To meet the ultra-high performance requirements of the DoD in High Speed Data Storage and Retrieval, priority should be given to support of areas of particular relevance to DoD needs not being addressed by industrial research activities in the area of magnetic recording and Magneto-optic recording.

In setting up a magnetics R&D program for the DoD, priority should be given to funding magnetics research at universities. This is needed to restore an adequate level of advanced magnetics education to meet future DoD manpower needs (manpower in the magnetics area is in especially short supply in the U.S. with regard to both quantity and quality). Support should be provided to outstanding research programs carried out by small research groups at a variety of universities as well as by larger groups at the two newly established Magnetics Centers at Carnegie Mellon Univiersity and the University of California at San Diego.

AGENDA

WORKSHOP ON MAGNETISM AND MAGNETIC MATERIALS

July 21-22, 1986
La Jolla, California

Organizers: M. S. Dresselhaus, H. Ehrenreich, G. Vineyard

Monday, July 21

Opening Remarks/Welcome, M. S. Dresselhaus (MRC and MIT)

Overview of Opportunities and Needs of the DoD in Magnetism and Magnetic, Materials, N. C. Koon
(NRL)

New Magnetic Materials; Frontier Research Prospectives, J. F. Herbst (UCSB)

Epitaxial Magnetic Films on Semiconductors, G. A. Prinz (NRL)

Artificial Magnetic Multilayers, M. B. Salamon (U Ill.)

Modeling and Predictions of Magnetism in Bulk, A. J. Freeman (Northwestern U)

2D Magnetism in Graphite Intercalation Compounds, G. Dresselhaus (MIT)

Surface Magnetism - Experimental Studies Using Electrons, D. T. Pierce (NBS)

Free Discussion

Tuesday, July 22

Magnetic Materials for Recording and Other Applications, R. White (CDC)

Problems in the Analysis of High Density Magnetic Recording Limits, N. Bertram (UCSD)

1. Magneto-Optic Recording
2. Vertical Bloch Line Memory M. H. Kryder (Carnegie-Mellon)

Wrap-Up (M. S. Dresselhaus)

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SELF-ASSEMBLY OF MATERIALS

G. M. Whitesides and M. S. Wrighton

INTRODUCTION

The availability of materials having required levels of performance increasingly limits the capabilities of DoD systems. Systems designers have been through a period in which developmental improvements in existing materials --- particularly conventional metal alloys for structures, and silicon-based microelectronic devices for computation --- supplemented with small-volume specialty materials have satisfied their requirements. Systems now proposed specify levels of performance that frequently seem difficult or impossible to meet using existing materials or readily achieved improvements on these materials. The generic requirements that exceed the performance of existing materials are for:

i)   Light structural materials that retain their strength at high temperatures (for advanced aircraft, engines, and space structures).

ii) Ultratough and ultrahard materials (for armor).

iii) Materials (and more importantly manufacturing and processing technologies) capable of producing very small, defect-free structures (for small, low-power microelectronic devices and sensors).

The current set of materials classes --- ceramics, intermetallics, metals, and polymers --- as single, homogeneous materials, often do not meet the requirements even for existing systems, and combinations of them -- composites -- are used to provide improved properties. In fact, one of the major current activities of materials science and engineering is the assembly of complex materials and structures involving many different components. The assembly (or processing) of these multicomponent systems follows two broad strategies: "Man-assembly" -- that is, the designed fabrication of the systems

ASSEMBLY OF MULTICOMPONENT SYSTEMS

Man-Assembled	Self-Assembled
Fiber-reinforced composites	Phase-separated alloys
Microelectronic structures	Phase-separated polymers
Multilayer barrier films	Liquid-crystal polymers
Low-technology products:	Biological systems
concrete, carbon black-toughened rubber	

-- and "Self-assembly" -- in which the material spontaneously develops the required multicomponent structure without fabrication or with relatively simple processing.

The first of these two strategies has received the most extensive recent development, and high-performance fiber-reinforced composite aircraft parts and multilayer microelectronic devices provide examples of the performance and complexity that can be generated using this strategy. The processing required in the assembly of structures using this strategy is, however, almost necessarily complex and expensive, especially when very high degrees of structural perfection (or low levels of defects) are required. By contrast, processing of self-assembled structures may be considerably less complex and expensive, although, in general, the degree of control achievable using this strategy has been significantly lower than achievable by "man-assembly".

There is, however, the suggestion in biological systems that there are unexplored and potentially practical strategies for self-assembly that would make possible the construction of multicomponent systems without external control. Biological systems are self-assembling (in the sense that external fabrication is not required, although energy certainly is), and they achieve levels of complexity and performance (of certain types) that are not matched by any man-assembled systems.

The objectives of this workshop were:

- To examine a number of types of systems that exhibit the ability to "self-assemble" or "self-organize", including biological systems, and to identify strategies or systems that might provide the basis for new or improved materials or materials processing technologies relevant to DoD interests.

- To identify the science base that would have to be developed in order to generate new strategies based on self-assembly, or to improve, control and extend existing strategies.

To summarize:

The Problem:

- Proposed DoD systems require materials performance that cannot be met by existing materials systems.

- Processing of existing and proposed systems is often difficult and expensive, and is a significant source of defects that limit performance.

The Motivation for the Workshop

- A number of systems ranging from simple inorganics (colloids) to complex biologicals (cellular components, whole cells, complete organisms) display an intrinsic ability to organize themselves into complex structures, some having remarkable and potentially very useful properties, without external processing.

- These systems may provide strategies or materials of use in DoD applications.

Objectives

- To define the science base required to develop materials for DoD applications based on the strategy of self-assembly.

- To identify particular materials technologies to which strategies based on self-assembly can be applied to give new or improved materials, and to simplify processing procedures.

- To explore the possibility of producing classes of materials with structures presently not obtainable by existing methods.

- To identify specific classes of components (molecules, small particles) that will spontaneously form complex structures that are _functional_ (that is, have useful characteristics) and _robust_ (that is, will withstand plausible conditions to be encountered in a systems application).

The workshop included summaries of eight areas:

- Biological Structures and Systems
- Phospholipid-based Microstructures, Especially Tubules
- Micellar Liquid Crystals
- Phase-Separated Polymers
- Ordered Colloids
- Dendritic and Fractal Structures
- Chemical Reactions Showing Spacial or Temporal Organization
- Unusual Molecules and Systems: "Starburst" Macromolecules and Integrated Chemical Systems

In the sections that follow we summarize the areas of greatest significance in self-assembly of materials.

BIOLOGICAL SYSTEMS

There are two reasons to look carefully at biological systems: first, to examine the strategies used in biology to accomplish the self-assembly of the cell, with the intent of applying certain of these strategies for self-assembly to other, non-biological classes of components; second, to use biologically-derived molecules or close analogies of these substances as components in self-assembling systems. Self-assembly is ubiquitous in

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biology. At every level of organization, cells display a wide range of self-assembled structures.

Examples include:

DNA double helix

t-RNA

Domain structures in proteins

Protein-protein aggregates

Lipid bilayers

Microtubules and other components of the cytoskeleton

Vesicles and Organelles

Complex composite structures
(bone, teeth, tendon, blood vessel)

Complex functional structures
(muscles, kidney, liver)

Complex sensory structures
(eye, ear, organs of taste, touch, pain, heart)

Complex information processing systems
(nerves, brain)

Biological structures use a surprisingly limited number of types of chemical interactions in self-assembly. The general principle of biological self-assembly is to put together the structures of interest (at least at the molecular level) using a large number of relatively weak bonds rather than a small number of strong bonds. The origin of this principle lies in the particular strength and special requirement of biological systems: that is, extremely discriminating molecular recognition. The inside of a cell contains many thousands of chemical compounds, and the first task in organization of such a system is to be able to distinguish the individual components. Only a few different types of bonds can be formed reversibly under the conditions encountered in living cells: van der Waals bonds (typically having energies of the order of 0.1 eV), hydrogen bonds (typically 0.2-0.3 eV), and disulfide bonds (typically 2 eV). These last are used relatively

rarely, and then only in circumstances in which recognition is not required. For comparison, the average kinetic energy of a molecule is 0.02 eV at room temperature.

The criterion of reversibility in association is critical for molecular recognition: a molecule must be able to recognize and reject an inappropriate candidate for association when encountered by random diffusion, and will be able to do so only if the interaction between the two colliding molecules is strong enough to permit recognition but weak enough to permit dissociation and escape. If the interaction between biological molecules were based on the formation of one or two strong bonds, it would be difficult to make many differentiations. If the interaction comprised the sum of a number of weak bonds (as, for example, in the van der Waals interactions between two large molecules able to fit together closely by virtue of complementary shapes) the sum of these weak interactions would be large enough to produce stable associations if all are effective $(\underline{1} \rightarrow \underline{2})$ but would be weak if only a few of the potentially interacting groups "match" $(\underline{1} \leftrightarrow \underline{3})$.
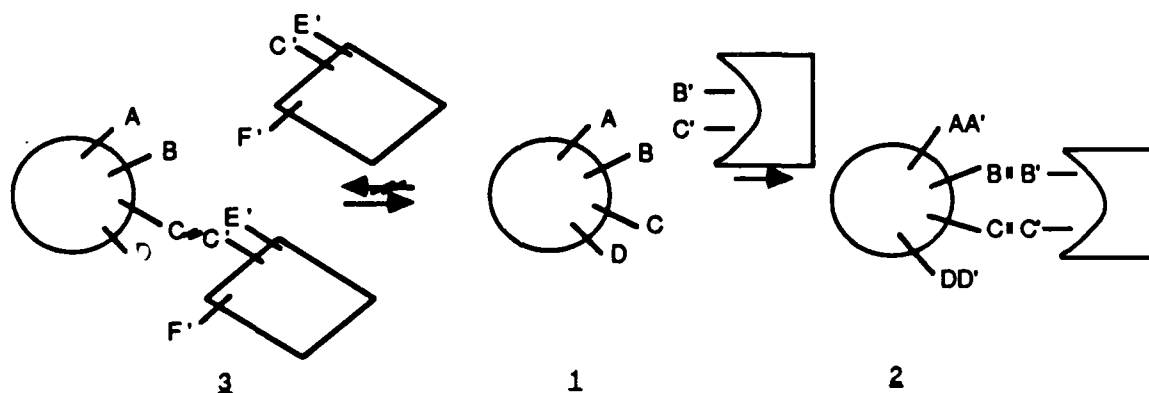
Probably the most important lesson to be drawn from biology concerning self-assembly is the power of systems of molecular recognition based on multiple weak interactions between molecules that are exactly complementary in shape. This strategy is, of course, quite different from that used in much of materials assembly, in which strong bonds are used. The biological systems do, however, have uniquely difficult and

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demanding problems in recognition: sensitive recognition is not as serious a problem in most areas of materials science.

A second important consideration in biological systems is the environment in which they must operate: aqueous solution, pH 7, 0°C - 100°C, usually in contact with oxygen. Two issues follow from these environmental constraints. First, biology relies heavily on so-called hydrophobic interactions to provide recognition and structure. Hydrophobic interactions are a consequence of the tendency for non-polar structures that cannot form hydrogen bonds to be excluded from water (and thus forced into association with one another). The simplest illustration of the hydrophobic effect in operation is the insolubility of benzene in water: benzene molecules are excluded from the aqueous phase, not because water molecules repel benzene, but because water attracts water much more strongly than water attracts benzene.

The importance of the hydrophobic bond in biological systems is substantial, but this type of bond probably will not be applicable to many other (non-aqueous) systems. Thus, strategies used to provide recognition in water in biological systems may not be directly usable in non-aqueous systems (although it may be possible to develop analogs of the hydrophobic effect to use in other non-aqueous systems).

A second constraint in biological systems is the limited range of temperatures typically encountered in them. The free energy ΔG of a process of interest is a balance of enthalpic (ΔH) and entropic (ΔS) factors. In biological systems, both typically contribute significantly to ΔG, Eq. (1).

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

Many of the important problems in structural materials involve systems intended for operation at temperatures of 1500-2000°C. Entropic factors that are relatively unimportant at 32°C can be very important at 1500°C, and the balance between entropy

and enthalpy achieved in biological systems during self-assembly cannot be directly transferred to systems intended to be self-assembled at 1500°C. (There is, of course, no objection in principle to assembling a system at low temperature and then processing it into a form stable at high temperature).

Biological systems thus provide a wide range of model structures that suggest strategies for self assembly, and a large number of molecules that spontaneously self-assemble. It will provide a rich and stimulating source of concepts and hypotheses for self-assembling systems, but the constraints imposed by the aqueous environment and by the modest temperatures encountered must be kept clearly in mind in the design of new systems based on biological models, and in the use of biological components in non-biological applications.

PHASE SEPARATED POLYMERS

One of the most promising materials systems that exhibit self-assembly are phase -separated polymers. Figure 1 shows schematically the concept of a phase-separated polymer showing how a block co-polymer can undergo a kind of phase separation leading to a solid consisting of domains of material of one or the other of the constituent polymer materials. An example of a system that should exhibit such phase separation would be a block co-polymer of polystyrene and poly(1,3-butadiene). The general concept is that the poly(1,3-butadiene) and polystyrene will tend to be immiscible leading to phase separation even when the two polymers are linked in a linear diblock architecture. Such phase-separated polymer structures may be useful "as is" or treated after phase separation to make one domain more rigid. For example, heat treatment or ultraviolet light can be used to promote cross linking in one of the domains. Phase-separated polymers may thus be useful in fabrication of composite structures having improved mechanical properties.

PHASE-SEPARATED POLYMERS
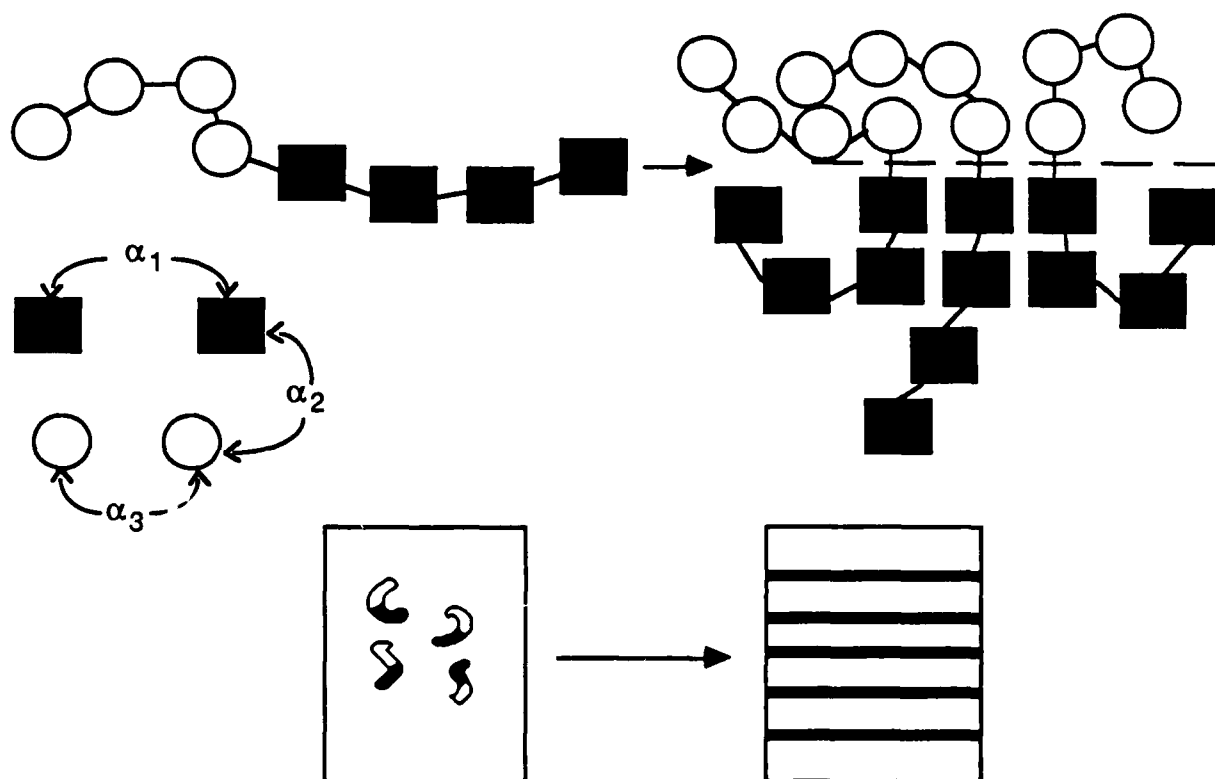
APPLICATIONS

SELF-ASSEMBLING COMPOSITES

Figure 1.

The spontaneous separation of two immiscible phases is a commonplace phenomenon. However, surprisingly relatively little detailed knowledge is available concerning such simple phase separations. There is the organic chemist's adage that "like dissolves like" but precisely why, for example, benzene does not dissolve in water is a question that can not be confidently resolved in detail. The prospects of interesting materials properties from phase-separated polymers is a relatively recent realization, and the detailed investigation of the fundamentals of superficially simple phenomena is

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just now becoming regarded as a high payoff research activity. It is already clear that a wide range of self-assembled potentially useful structures can be achieved depending on conditions and the nature of the polymer. A central issue is to be able to develop the thermodynamics applicable to making predictions concerning the structure of domains formed by phase-separated polymers. It is important to recognize that the thermodynamics will depend not only on the elemental compositions and nature of the monomers of the polymer but also on the system architecture (homopolymers, random polymers, block copolymer). The polymer chemist's adage concerning miscibility is that "nothing dissolves anything" but the detailed elaboration to predict the nature of structures produced by phase separation is not easy.

There is evidence that new polymer morphologies can be achieved as a consequence of phase separation. It will be important to establish whether the new morphologies result in structural materials having superior mechanical properties. Some of the systems are too new to have been evaluated, but progress in making the connections between the structure and mechanical properties is needed. The novel structures that can be achieved via phase-separated polymers will certainly produce new kinds of composite systems that are produced more efficiently than existing conventional systems such as fiber/matrix composite, but the composites derived from phase-separated polymers have yet to be fully characterized. Indeed, the field is in its infancy and more research will be required in order to produce the optimum materials. There is a particular need to develop processing procedures to do post treatments (heat, photochemical, chemical, etc.) that yield durable structural materials.

Aside from the most promising applications associated with structural composites there are potentially other useful applications of phase separated polymers. The regularity and dimension of the inhomogeneity of the polymer materials suggest that there may be opportunities in microfabrication of electronic devices. There may also be

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ways to exploit post treatments in a way that allows easy fabrication of membranes having chemically functionalized pores and pores of controlled dimension.

ORDERED COLLOIDS

Spontaneous ordering of small spherical particles is a second kind of self-assembly that has been demonstrated and has potential significance in the preparation of materials having structural or other functions. The beautiful visible light diffraction giving opals their brilliance is now known to be associated with the ordered arrangement, in three dimensions, of naturally occurring, spherical SiO_2 particles having a very narrow size distribution. Visible light diffraction of "crystals" of spherical particles of dimension of the order of the wavelength of visible light is analogous to X-ray diffraction of ordinary crystals in that the atoms in ordinary crystals are separated by a dimension of the order of the wavelength of X-rays. Figure 2 shows a schematic representation of randomly oriented, spherical particles and a crystalline array of such particles that can be taken as an illustration of an ordered colloid. The spontaneous ordering of small, spherical ceramic particles can be useful in preparing ceramic objects having smaller voids which are more uniformly distributed in the final ceramic object formed in the sintering process. More complex structures derived from ordered colloids may give additional improvements by lowering void formation, reducing shrinkage in the sintering process, and reducing the temperature required for sintering.

In the early studies of ordered arrangements of microspheres the crystallization was a consequence of repulsive forces between the particles as a consequence of fixed charges on their surface. At the present time there are now known many mechanisms for inducing order in two dimensions, typically at interfaces. Studies of such ordering mechanisms have fundamental significance in the sense that such systems allow investigation of "crystal" growth and the imperfections in such processes. In practical

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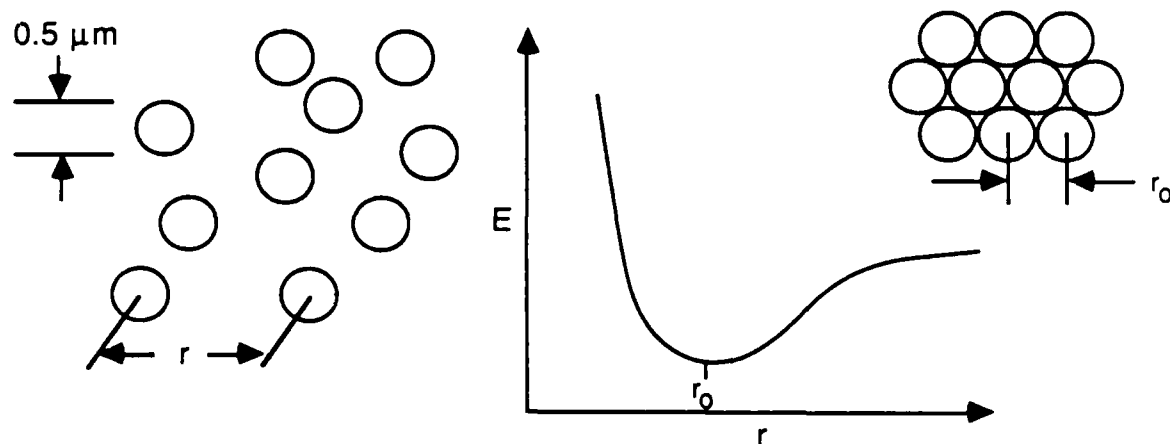
ORDERED COLLOIDS

APPLICATIONS

CERAMIC (METAL?) PROCESSING
COATINGS
OPTICAL SYSTEMS

Figure 2.

terms, ordering of colloidal microspheres in two dimensions can be important in

producing conformal, highly ordered coatings. Post-treatment procedures could then

yield scratch and corrosion resistant films or barrier coatings. Highly ordered

mono-grain films of particles may yield other important properties as well. These may

include applications in solar energy conversion and in electrochemical processes,

where the monograin film is a semiconductor or catalyst in contact with a conducting

substrate. The elaboration of the types of ordered colloids is likely to be an important

aspect of materials self-assembly, because inorganic materials, such as SiO_2, obviously

offer the prospect of high temperature materials of technological significance.

As the mechanisms for inducing order in colloids are understood it is likely that a

large number of improved materials systems will emerge. One of the interesting

developments is likely to involve three dimensional ordering of ceramic particles initially present in two sizes, each with a very narrow size distribution. The objective is to crystallize the different size spheres as in a conventional ionic lattice (cation, small; anion, large) in order to rationally reduce the void volume in the solids. The sketch below illustrates the essential idea. The small and large spheres could be of the same material to produce relatively void free ceramic upon sintering. Different materials could be achieved if the small and large spheres are of different composition. Spontaneous
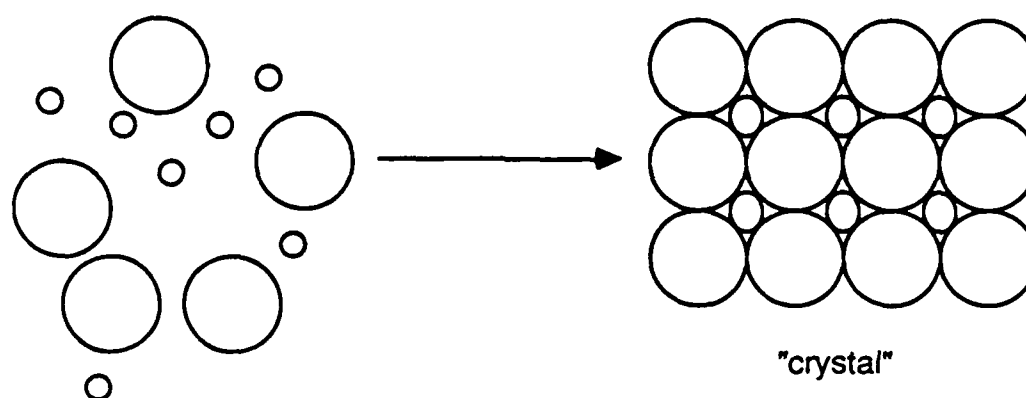
"crystal"

crystallization, as sketched above and in Figure 2, occurs and offers the prospect of studying fundamentals of crystallization in a new way, because the dynamics of the process can be studied in real time by optical microscopy. Aside from the expectation of enormous practical consequence, there is good reason to expect advances in fundamental understanding that have application to areas of conventional crystal growth.

Producing the microspheres for ordered colloids in a narrow size distribution is already showing economic payoff in separations science. Highly efficient chromatography columns can be produced using uniform particle size in the packing material. The potential rewards in structural materials from ordered colloids justifies the considerable effort involved in producing the monodispersed particle size.

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MONOLAYERS

The spontaneous organization of molecules initially dissolved in a solution can occur, as represented in Figure 3, such that a surface immersed in the solution becomes coated with a close-packed, highly ordered, array of the molecules. The immersion of

MONOLAYERS

10-30 Å
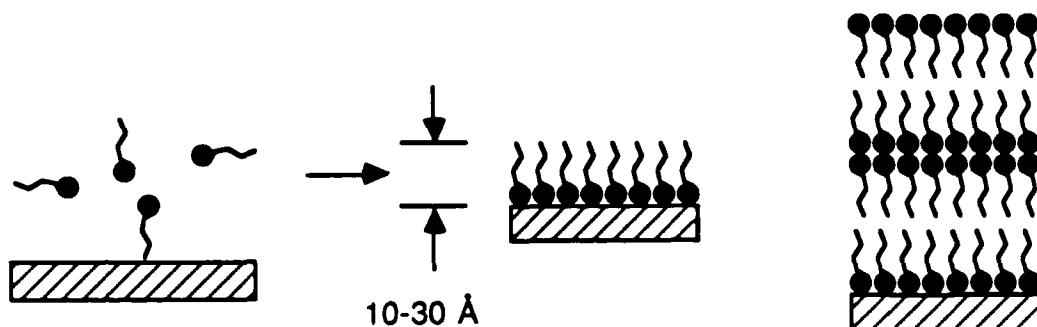
APPLICATIONS

Interface control in composites
Barrier films: corrosion, diffusion
Anti-friction
Microelectronics
    Thin film dielectrics
    Adhesion control agents in packaging
Optics: Anti-reflective; control of index of refraction

Figure 3.

the surface into the solution containing the molecule results in the spontaneous self-assembly of the monomolecular layer. This procedure for forming a monolayer differs from the Langmuir-Blodgett technique in that the molecules initially present are

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randomly distributed in the liquid solvent. There is a degree of self-assembly in Langmuir-Blodgett techniques also, but the ordering of monolayer forming molecules is typically first achieved at a liquid/air interface and the monolayer is then transferred to a solid substrate by holding the ordered film at constant pressure as the film is transferred. The Langmuir-Blodgett technique is presently best for producing highly ordered multilayer assemblies of monolayer forming molecules, but the spontaneous self-assembly of a monolayer onto a surface has many applications and illustrates, in a very simple fashion just how important and easy self-assembly of materials can be.

A specific example of the spontaneous self-assembly of a monolayer onto a surface involves the formation of a monolayer of $HS(CH_2)_{10}COOH$ onto Au. A key to the spontaneous self-assembly is that RSH interacts strongly with the Au, the -SH group orients the molecules and can be said to coordinate to the surface of Au much as the ligating atom of a ligand interacts with a metal center in a discrete transition metal complex. The long chain of $-CH_2-$ units in $HS(CH_2)_{10}COOH$ is a typical functionality associated with synthetic molecules which order into monolayers. Presumably the "hydrocarbon phase separation" in monolayers is analogous to phase separation in polymers, but as in most of these systems the ability to quantitatively assess just what molecular structure is required to bring about order is not available. Clearly, the Au/S interaction contributes to the ability to overcome the disorder in the solution of $HS(CH_2)_{10}COOH$, but the ability to form highly ordered films of long chain molecules likely involves other factors as well. It is quite likely, though, that interaction of the solid substrate with the molecules in solution will allow the self-assembly of ordered molecules with a very wide range of molecules that would not ordinarily form close packed monolayers under any other circumstances. The point is that the energetics of coordination to the surface may overcome the tendency to disorder. Accordingly, there is considerable merit in developing the coordination chemistry of surfaces, in order to be

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able to rationally prepare a wide range of surfaces modified with a close-packed monolayer.

The applications of self-assembled monolayers are quite broad and depend, of course, on the nature of the molecules actually used. Specific illustrations of improvement in adhesion of polymers to surfaces involves first modifying the surface with a molecular assembly where the molecules terminate in a functional group that can be incorporated into a polymer film. Such a procedure yields a method to bond polyethylene to Au where the adhesion layer is a monolayer of $HS(CH_2)_n CH = CH_2$. A similar strategy has been employed to improve adhesion of polypyrrole to Si where the adhesion layer is derived from the pyrrole derivative:
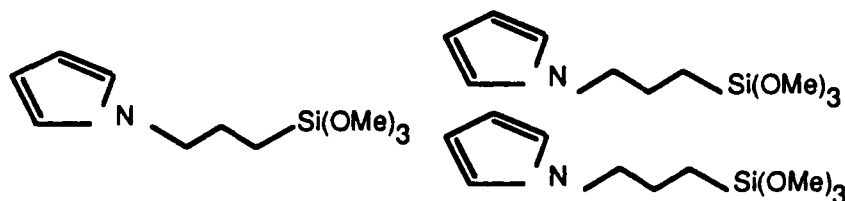
The $-Si(OMe)_3$ group provides a way to bind the polymerizable group to the surface. Diversity in the link to the surface, the connecting chain, and the group anchored to the surface can be large. A wide range of applications of self-assembled monolayers can thus be envisioned including barrier films; anti-friction, reflection and corrosion coatings; films for interface control in structural composites; adhesion control films; and thin film dielectrics in microelectronic devices.

TUBULES

The formation of "tubules", Figure 4, illustrates the self-assembly of an object which is significantly larger in all outer dimensions than the constituent molecules which are used to prepare the tubule. Molecules (extended length ~20Å) monolayers,

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micelles, and vesicles have been discovered to self-assemble in a manner that yields tubules of dimensions of ~0.5 μm in diameter and >10 μm in length (up to mm's). The tubules are thought to be hollow with a thin wall. The molecular building blocks are synthetic phospholipid molecules having long chain hydrocarbon tails that include a diacetylene unit. The significance of the diacetylene function in the hydrocarbon chain is that photochemical treatment of the tubules leads to covalent, intermolecular links that endow the tubules with considerable durability. Thus, molecular materials can self-assemble to yield relatively large objects having unique structural properties. Post treatment gives robust objects that have a large number of potential applications stemming from the tubular structure of the self-assembled object.

TUBULES
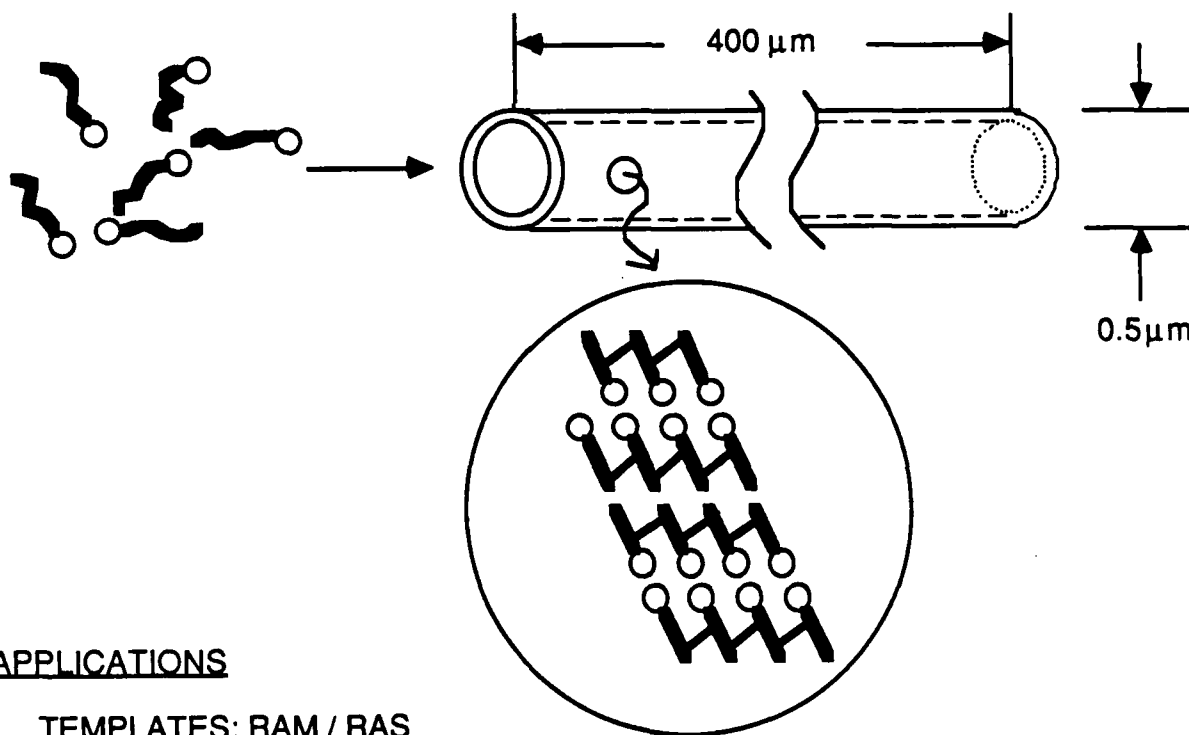
APPLICATIONS

TEMPLATES: RAM / RAS
ACOUSTIC SENSORS
DYE LASERS

Figure 4.

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Tubules self-assembled from molecular subunits raise important fundamental questions. Why is a tubular structure formed? The ability to predict the structure of an assembly hinges on the ability to understand how the structure of the constituent molecules influences the structure of the assembled object; it is presently not possible to "design" molecules to assemble into a tubular structure. Fundamental aspects of the growth mechanism and the thermodynamics of the process are not understood. In general, the self-assembly of long chain hydrocarbon molecules with a polar head group is an area that has received much attention, but there is still relatively little predictive ability with respect to whether one structure or another will be assembled. If vesicles are to be formed, what will be their size? Will they be multilamellar or single walled? It is fair to note that the formation of tubules was an unanticipated result. Given the surprising formation of tubules and the lack of predictive power in connection with even simpler systems there is the possibility that presently unknown supermolecular structures remain to be discovered.

The unique structural properties of phospholipid tubules suggest applications that justify effort to understand, more efficiently prepare, and modify the tubules. The tubular structures have large anisotropy and aspect ratio and there is the expectation that the inner and outer surface will have different chemistry. Considering their size, shape, and density, the coating of tubules with thin metal films offers a way to improve performance of RAM/RAS materials. Similar considerations also make tubules of potential significance in sonic and ultrasonic microphone applications. The demonstrated ability to orient the tubules is crucial to such applications.

KINETICALLY FORMED STRUCTURES

There are many situations where kinetics can control the formation of an ordered system. For example, spatial order from complex chemical reactions occurring in

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solutions has been known for many years, but detailed investigations of such systems have not been pursued from the standpoint of self-assembly of materials. In general, oscillations of chemical species in time and space can occur when there are mechanisms for kinetic feedback. The consequences of such kinetic feedback are observable in the material world in macroscopic and microscopic respects. For example, the rise and fall of the population of kinds of living systems is one consequence of such dynamics; natural food supplies are generated at a certain rate, the population grows and consumes the food, with a diminished food supply the population falls, the food supply then grows allowing the population to rise again and so on. Of more direct relevance to solid materials are examples of precipitation processes where concentration variations in space can be brought about through depletion via precipitation and diffusion. In some instances surprisingly modest feedback can produce large effects as in solubility changes in response to local temperature changes associated with a precipitation process. Figure 5 shows an example of the kind of spatial order that can be achieved from a simple chemical reaction.

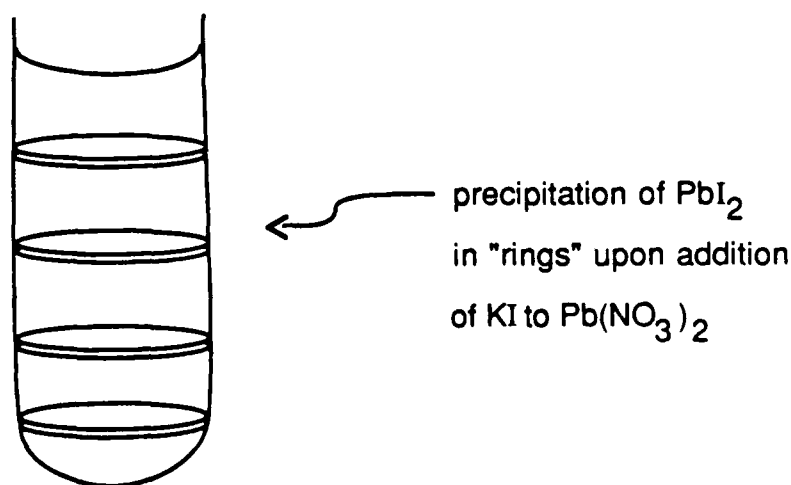precipitation of PbI_2 in "rings" upon addition of KI to $Pb(NO_3)_2$

Figure 5. An illustration of spatial order in a simple precipitation process.

Another kind of ordering of materials can be illustrated with an example of an electrochemically driven reaction. It has been demonstrated that a metal film can be deposited <u>inside</u> a redox polymer coated onto an electrode as sketched below (<u>J. Phys. Chem., 1986, 90</u>, 1367).

redox polymer ⟶ ～～～～～～ reduce ⟶ ＝＝＝＝＝＝ ⟵ Ag film
electrode ⟶ //////////// ////////////

The key to achieving the structure is that the diffusion coefficient for carrier transport through the redox polymer is different than for Ag^+. Accordingly, upon stepping the electrode potential to a reducing value the Ag^+ ions "meet" the diffusing reducing equivalents inside the polymer at a reasonably well-defined position in the film. There are many other situations where electrochemical growth procedures could be used to easily prepare complex structures which have electronic, sensing, or energy conversion functions.

Another area involving complex kinetics is the formation of dendritic structures and a subset of these can be fractal. In principle, fractal dendrites can also have some elements of symmetry when grown with certain boundary conditions. Control of dendrite formation is crucial to the improvement of the rechargeability of batteries based on the electrochemical deposition of metals, to provide a practical application area where kinetic control over the morphology of the solid material has not been achieved. It is not clear that characterization of the complex morphology of solids with fractal dimensions is useful in controlling (or even predicting) morphologies, but it does appear to be true that there is value in such characterization. Modelling the formation of complex solid structures is certainly a worthwhile endeavor when coupled to experiments where realistic boundary conditions can be varied.

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Aside from gaining insight into growth of materials the study of spatial and temporal order in chemical reactions can be quite useful in improving chemical processes involving a sequence of complex, coupled chemical reactions. There are applications of fundamental studies in complicated reaction dynamics to achieve maximum efficiency from large scale chemical reactors, to better understand and control crystal growth, heat transfer, and explosives and perhaps to design new kinds of sensors.

RECOMMENDATIONS

Two types of opportunities present themselves in the area of self-assembling systems: Those that apply or develop the concept of self-assembly in existing materials systems to improve their properties, and those that develop the science and technology base for self assembly.

Applications for Existing Ordered Systems

1. Phase-Separated Polymers promise to be an important class of structural materials, and the principles being developed in structural materials may eventually be extended to materials having other functional properties (for example, a chromophoric dye-containing phase in a transparent host polymer would find use in optical systems). The requirements in this area are to understand in predictive detail the factors leading to phase separation and determining the shapes and order of the separated phases, to develop an understanding of the relation between component structure and macroscopic properties, and to develop new polymer systems based on phase separation. A system in which phase separation could be induced following injection molding, and one of the two phases could be crosslined to a rigid strong phase while leaving the second phase rubbery would in principal lead to injection moldable fiber-reinforced composites.

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2. <u>Ordered Colloids</u> seem a highly attractive precursor to high-performance ceramics and perhaps for metals. The ability of monodisperse, spherical colloids to pack into dense, imperfection-free structures is well established. These structures formed from a monodisperse spherical alumina should lead to highly perfect, void-free ceramics, but the improvement in properties to be obtained by this procedure remain to be firmly explored experimentally. A next level of organization would be to develop systems containing a mixture of <u>two</u> monodisperse spheres, the smaller capable of packing in the voids in the larger. This type of crystallization might be helped by fixing opposite charge types on the spheres. These types of systems should exhibit much smaller degrees of shrinkage on sintering than conventional systems.

In principle, the same ideas should be applicable in powder metallurgy, and in making metal and ceramic alloys.

<u>Science/Technology Base</u>.

The area of self assembly is an enormously exciting one, and the list of worthwhile topics is longer than is appropriate to list here. The following should be considered representative, and illustrative of areas relevant in some interval of time to DoD concerns.

1. <u>The materials science of monodisperse components</u>. Monodisperse sphere have been shown to have remarkable properties in self-ordering. What are the properties of monodisperse cubes or rods? How can any of these systems be made practically?

Practical syntheses will probably emerge from colloid and emulsion chemistry. We note as an example of an application that self-organizing monodisperse ceramic cubes should give a "green" structure with zero void volume, and should sinter at very low temperatures.

2. <u>Monolayer and Multilayer Systems</u>. The principles underlying these assemblies are now emerging and good synthetic methods are being developed. These types of assemblies are on the verge of becoming a technology (for controlling wetting, adhesion, and tribology; as thin-film dielectrics and insulators; in optical devices for controlling index of refraction) but it is important to develop more robust and complex molecular components. Phthalocyanines and fluorocarbons are particularly attractive.

3. <u>Kinetic Structures</u>. The study of complex systems with extensive feedback is just emerging as a productive and scientifically tractable discipline. This area will find applications in areas such as explosion propagation, crystal growth, and pattern development.

4. <u>Phase Separation; Ordering</u>. The fundamental chemistry and physics underlying both phase separation and ordering remains poorly understood. When will two liquids phase separate? How does one design new liquid crystal systems? What would be the order in a system of monodisperse disks with mutually repelling surface charge? None of these or a variety of related questions can now be answered. We note a particular need for <u>realistic</u> theory in this area: that is, a theory capable of calculating and incorporating system entropies.

5. <u>More Complex Strategies for Assembly</u>. The technology of self assembly is at very primitive point, relative to the potential suggested by biology. The present state of the art is represented by the phospholipid tubules, which spontaneously self-assemble from molecules. What is required to have these tubules self-assemble further: for example, into an open hexagonal lattice structure?

6. <u>Structural Biology</u>. Biology contains an enormous number of self-assembling structures. The examination of the principles on which these self-assembly processes are based from the vantage of materials science would yield a number of strategies that might be transferred into improved techniques for processing of existing materials.

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Study of these biological systems (proteins, structured protein aggregates, lipids, organelles, specialized functional or sensory organs) may also yield components of direct use in materials applications.

APPENDIX A.

AGENDA

WORKSHOP ON SELF-ASSEMBLY OF MATERIALS

July 23-24, 1986
La Jolla, California

<u>Purpose of the Workshop</u> - The purpose of the workshop is to present and discuss the basic science needed to synthesize, by <u>self-assembly</u>, complex, durable materials and materials-based systems having new and interesting properties. A diverse group, consisting of invitees and members of the Materials Research Council, will have a day and a half meeting with approximately 50 percent of the time devoted to formal presentation and the remainder devoted to discussion. Members of the Materials Research Council will prepare a report to assess the field and identify areas of significant scientific opportunity of relevance to DARPA.

<u>Wednesday, July 23</u>

<u>Session I</u>   M. S. Wrighton, Chairman

Overview of Biological Structures and Functions, G. M. Whitesides (Harvard)

Novel Structures in the 1μm Size Regime from Self-Organizing Molecules,
    Joel Schnur (NRL)

Physics of Micellar Liquid Crystals, J. David Litster (MIT)

<u>Session II</u>   G. M. Whitesides, Chairman

Phase Separated Polymers, Frank Karasz (U. Mass.)

A New Class of Polymers: Starbust Dendritic Macromolecules,
Don A. Tomalia (Dow Chemical)

<u>Thursday, July 24</u>

<u>Session III</u>   H. Kent Bowen, Chairman

Spatial and Temporal Order in Chemical Reactions, John Ross (Stanford)

Physics of Ordered Colloids, George Onoda (IBM)

Integrated Chemical Systems, Allen J. Bard (UT)

Fractal Aggregates: What They are and How They Grow, Paul Meakin (DuPont)

APPENDIX B.

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SPECIAL MATERIALS FOR UNDERWATER ACOUSTIC APPLICATIONS

J. L. Margrave

Most of the applications of plastics and polymers in underwater acoustics are very sensitive to surface properties, toughness, and permeability to H_2O and other species. A review of materials needs in underwater acoustics has been provided by Ellinthorpe.[1]

Several of the problems cited can be resolved by the use of fluorinated films as described by Margrave and Lagow.[2] The "Lamar" process produces a chemically adherent film of selected thickness on various hydrocarbon-based polymers (polyethylene, polypropylene, polystyrene, polyvinyl chloride, natural rubber, neoprene, etc.).[3] This film both enhances the chemical corrosion resistance, increases thermal stability and the flammability limit and the fluorocarbon surface is not wet by water.

Hermeticity

According to Ellinthorpe, there is a widespread need for a durable waterproofing coating with a long life. The direct fluorination of a snugly fitted polymer cover should provide this property. Not only will the corrosion resistance and thermal stability be enhanced but also, the permeability of the polymer to H_2O, O_2, CO_2, etc. is dramatically reduced. Quantitative testing of some surface fluorinated polymers is recommended.[3]

Toughness

The neoprene exterior surface of acoustic sensors can probably be improved by providing a fluorocarbon surface/coating. The useful lifetime in sea water should be further extended and the coating has a low frictional coefficient which should help to slide along a pier with minimal damage. The fluorocarbon layer can be fairly thick

and mechanically strong, depending on the substrate. Tests of real fluoro-coated objects is recommended.[3]

Transduction

Although fluorination of ceramic devices is not practical, it should be possible to enhance the thermal stability of PVF_2 by surface fluorination. Thus, if a thin layer of perfluoro-carbon can be applied by direct fluorination at ~25°C without (damaging) the piezoelectric properties, one would expect to find improved thermal properties of the PVF_2. Obviously, some careful studies of PVF_2 sensors, with and without the coating, over a range of temperatures appears desirable.[3]

SUMMARY

Direct fluorination of various plastics and polymers which are used in underwater acoustic devices is proposed. Corrosion resistance, higher thermal stability, water repellancy and reduced permeability are provided by these chemically adherent fluorocarbon films.

REFERENCES

1. A. Ellinthorpe, "Topics in Underwater Acoustic Materials," DARPA/MRC, 1986.

2. (a) J. L. Margrave and R. J. Lagow, U. S. Patent No. 3,674,432, July 4, 1972.

   (b) J. L. Margrave and R. J. Lagow, U. S. Patent No. 3,758,450, Sept. 11, 1973.

   (c) J. L. Margrave and R. J. Lagow, U. S. Patent No. 3,775,489, Nov. 27, 1973.

3. Fluorination of plastics/polymers can be arranged through Mar Chem, Inc., P.O. Box 6914, Houston, Texas 77265.

TOPICS IN UNDERWATER ACOUSTICS MATERIALS

A. Ellinthorpe

INTRODUCTION

There have been no major, system level, design changes in underwater acoustics for about 25 years; at that time there were major advances introduced almost across the board, which gave us a large margin of superiority over our opponent. That margin was preserved without any action on our part because he was careless in the quieting design of his submarines. In retrospect, it appears more accurate to say that he concentrated his attention on other performance parameters such as speed and depth, because his latest designs have shown step-like quieting improvements, and our "acoustic advantage" appears to have slipped away. Sweeping design responses are needed, and they are underway.

The design parameter that determines detection performance is the brutally simple size of the receiving antenna aperture. At present, shipboard acoustic antennas are small enough to be considered minor components by the ship's architect, but the required increase in size puts them into another category. Their cost will no longer be a negligible fraction of the overall ship cost, so lifetime becomes important. They will have to be integrated closely into the ship's structure, so isolation treatments of superior properties will be needed. They will constitute the outer surface of a large portion of the ship, so their skin must be tough enough to withstand the rigors of impacting tugs, piers, and debris and yet preserve its acoustic properties.

These needs are discussed below under the rubrics: Hermeticity, Absorptivity, Toughness, Reflectivity, Transduction. The ordering reflects a priority judgment.

Hermeticity

Not unexpectedly, there is a widespread need for waterproofing; hydrophones, electronics, optical fibers are examples of current interest. The key to a need for a fresh

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departure from current practices is the fact that the definition of "hermetic" has to include time as a parameter: it is guessed that lifetimes of at least one decade - perhaps two - will be needed to bring the system costs under control, a prospect that is currently well out of reach. Metals are said to be the only true hermetic barriers, but there are many underwater applications where they can't be used becaused of electrical conductivity, or weight, or electrolysis, or noise-making potential (e.g., oil canning), or bonding difficulties. Some sort of polymer solution is needed.

There are active developments in the retail packaging sector, viz. "plastic" soft drink containers. But I'm told that their concern is to keep out oxygen molecules, not water molecules, and that the latter is more difficult because the water molecule is polar. (That remark is hearsay quality: I am wholly uninformed.) I know of no active developments in the Navy.

Informed advice about the need (i.e., the problem) in the electronics and optical fiber areas can be obtained from Phil Danforth, an electronics person at NUSC in New London. Bob Ting is familiar with the need in connection with hydrophones.

Informed advice about the state of the relevant chemical arts (i.e., the solution) can be obtained from Ken Wynne, a chemist at ONR, and John Eynck, a rubber materials person with Westinghouse in Annapolis.

Absorptivity

The word is used here as to connote the need for an "anechoic" coating material, analogous to acoustic ceiling tile, that can be used to control reverberation in enclosed spaces. A specific problem stems from the fact that the only known way to isolate hydrophones from the noises in a ship's structure includes placing them a few feet away from the hull, a step that introduces a cavity that, like all cavities, exhibits resonances, and having wildly varying impedances at a sensor is inimical to a good response.

There has been a lot of work in this area, and it has the singular distinction of some analytic underpinning. A Hilbert transform relationship can be shown to exist

between loss factor and elastic modules functions of frequency. One of its meanings is that a homogeneous material can't satisfy the need: there has to be a frequency resonance of some sort, and this evidently means a system of inclusions in a host matrix. There is also implied a restrained frequency range of effectiveness, plus a corresponding concern in temperature that seems to be inherent in polymers.

The problem is made messy by the fact that it is a free-field propagating wave that we want to absorb. Loss in the body of the material can be represented as a complex propagation constant, a comment that (hopefully) brings out the intimation that the impedance of the material is also affected; if one wants to absorb, one must first get the adversary to enter the trap, which means one wants to preserve an impedance level the same as the water's. The dilemma is obvious. It is exascerbated by the firm requirement that the whole process has to be accomplished in a thickness of a very small fraction of a wavelength: only small units of inches are available for the coating, and the wavelength range of interest is in the tens of feet. Frequent reference to the success of ceiling tiles has to be made as goad.

Informed advice about the need (and on a whole related variety of topics) can be obtained from Nate Martin at BBN in Cambridge.

Lynn Rogers at Wright-Patterson runs a group that pursues damping materials for the Air Force, and the theoretical insight cited above came from him. (There is no contact between Navy-sponsored workers and Lynn Rogers.) But I believe that Lynn Rogers & Co. aren't concerned with free field waves, but rather with structural vibrations where impedance matching isn't a complication. Walt Madigosky at NSWC is believed to be the Navy guru who has done (and is doing) theoretical and experimental work in these matters. Steve Africk, of Atlantic Applied Research in Burlington (?) Mass., is a polymer materials engineering person (as distinct from chemistry) who did useful work in both analysis and experiment while he was (formerly) at BNN, and who is worth talking to.

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Ed Kerwin of BNN Cambridge is a father (grandfather?) figure who knows where every stumbling block lies, and is a wonderful conversationalist.

Toughness

The material currently used for the exterior surface of most acoustic sensors is neoprene; it doesn't ring like a metal, and its lifetime in seawater is among the best of the polymers - perhaps six years. It can't withstand a scraping load of the sort that is encountered coming alongside a pier, and the neoprene coated portions of a ship have to be treated with great care. In point of fact, the physical description of a scraping load is not defined; it involves a buckling deformation of the surface that is analytically troublesome and, within the Navy, at least, it has been shied away from and metals are viewed as the only materials that are macho enough to be acceptable.

I don't know of any active developments. Vinnie Godino, a structural person at BBN New London is aware of the issue, and is probably capable of formulating it in terms that could be a basis for a materials attack.

Reflectivity

There are aspects of acoustic control that require a reflective surface, the counterpart of an absorptive one. By itself, that is no problem; a sufficiently thick layer of gas will do fine. (acoustic impedances extend from light, elastic gases at one extreme to heavy, rigid metals at the other, spanning a range of about five orders of magnitude; water is about 1-1/2 orders of magnitude from the metal end, and about 3-1/2 from the gases.) The problem is that the gases have the disagreeable property of being compressive, a real drawback in submarine applications where the ambient pressure range covers about 60 atmospheres. There are, in fact, two distinguishable problems; materials commonly compress to the point where their acoustic properties vanish, or, more seriously, the associated change in the volume of displaced water can be enough to threaten the safety of the ship because it gets heavier as it descends.

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One possible solution, used in several experimental applications and about to see its first service trial, is to enclose the gas in a metal container and design that system to be resonant in the frequency range of interest. Unfortunately, for the frequency range of future interest (low hundreds of Hertz) the dimensions and weights turn out to be prohibitive. Another approach is to disperse gas bubbles in an elastomer matrix, and thus exploit a trade-off between compressibility and reflectivity. At the frequencies of interest, the thickness that is required to get reflectivity leads to prohibitive weight and volume.

Walt Madigosky of NSWC has laid the groundwork, both theoretical and empirical, for the bubbles in an elastomer, and Wayne Reader of NSRDC is believed to be the most prominent applications engineer. Steve Africk of Atlantic Applied Research has a lot of useful insights. Howard Schloemer of NUSC New London knows all there is to know about the resonant metal jacket approach.

Transduction

The sensing of acoustic waves involves the use of a device that converts pressure or velocity changes into electrical signals. In fact, no velocity sensors are used outside laboratories because they are excessively sensitive to incidental vibrations, an inevitable consequence of their superdirective property, which is analogous to an H field sensor in electromagnetics: but that is another long story that need not be confronted here - we'll be considering only pressure sensors.

Operational acoustic antennas are built like phased array radar antennas, for the same reasons, and so consist of a matrix or array of sensor elements. The arrays need to be densely packed to control grating lobe responses, so the morphology of the individual hydrophone elements should be similar to that of the parent array - a pancake or tile planar designs, a pencil for towed lines. Flexibility, toughness, lightness, long life are the obvious mechanical needs; high electrical output and an impedance matching water's are the electro-acoustic counterparts.

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All the materials in current widespread use are crystalline piezoelectric ceramics that have the drawbacks of being heavy and, worse, brittle; their use in these morphologies is out of the question. A good deal of laboratory scale work has been done seeking replacement formulations, motivated by the obvious brittleness problem and, while that has been solved in several ways, each of the solutions has unsatisfactory characteristics in some other respects. To render the balance of the discussion concrete, it is sufficient to note that those replacement approaches consist of two sets; one uses conventional piezo-active materials dispersed in some way in an elastomer matrix, and the other uses a novel material. The former set contains several members, differing chiefly in the graininess of the dispersed material, which ranges from small rods aligned like a forest of trees to powder-like flakes. The novel material set contains just one member, or variants of it; polyvinylidene fluoride, also known as PVF2 and PVDF.

A problem shared by all these competitors to conventional ceramics is inadequate electrical output. The device should be viewed as a generator, and like any generator, its output characterization requires at least two parameters, open circuit voltage and source impedance. Here, the open circuit voltage is the "sensitivity", a transfer function relating output voltage to input sound pressure; and the source impedance is measured simply by the capacitance because the resistive component is in all cases not a factor. The relevance of these measures lies in the fact that the device has to deliver enough signal to an amplifier to allow its design to achieve a satisfactorily low self-noise level. The figure-of-merit for the hydrophone device turns out to be the product of the capacitance and the square of the sensitivity (i.e., a power measure rather than voltage). An absolute value can be assigned because the amplifier's self-noise must be less that the noise present in the sea itself, and the devices under study fail this by a factor of three.

All these devices have, in some measure or another, an electrode adherence problem.

A possible problem, not yet fully explored, is the requirement that the sensitivity be constant over the entire surface device. If this is not satisfied, the wavenumber response (the Fourier transform of the spatial pattern of sensitivity) will not fall off at high wavenumbers and noise interferences will leak through. Some PVF2 samples have exhibited this defect, and it is presumably manifested in the dispersed ceramics.

PVF2 has a serious special problem, which is that its piezo-activity is irreversibly destroyed at relatively low temperatures. In early formulations this effect occurred at around 60 degrees Celsius, a temperature that is reached by the surface of a ship in Florida ports. A later formulation is able to reach about 100 degrees Celsius, which is satisfactory for service circumstances, but imposes troublesome restrictions on fabrication processes. A specific instance is the choice of waterproofing jacket material, whose curing temperature has to satisfy that bound, a fact that rules out many possibilities.

Informed advice about the electrical requirements can be obtained from Tim Straw, an electronics person at NUSC in New London. The materials as applied to hydrophones are familiar to Bob Ting of NRL Orlando, to Charlie Sherman at NUSC, and to Pat Welton at Westinghouse in Annapolis. The dispersed ceramic materials per se are familiar to Bob Penwalt in King of Prussia. The British, Thorne-EMI, have done a lot of good work of PVF2; in my opinion their people are better scientists than those at Penwalt but they are handicapped by our perceived need to have a domestic capability: Bob Ting can furnish their names.

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COMMENTS ON THE TOPICS IN UNDERWATER ACOUSTICS BY A. ELLINTHORPE

L. E. Cross

I agree strongly with the listing of major problem areas identified by Dr. Ellinthorpe. However, in assessing the priority for action, perhaps the urgency of need should be balanced with the opportunity for rapid progress in each of the areas of concern. In this context, I believe that for the transducer function, in the special area of polymer: ceramic composites, there is currently a unique "window of opportunity" which if not exploited soon may set back development of these promising materials quite seriously.

The juxtaposition of circumstances is as follows: Earlier DARPA/ONR funded studies have shown most interesting tailorable piezoelectric properties in macro-composite materials using specific internal connectivities in ceramics; polymer composites. For convenience, the original scaling was very coarse, however, recent development of high frequency electromechanical transducers have demonstrated that the same principles can be applied on much finer scales.

Industrial efforts to achieve these finer scales in practical materials for large area systems appear to be just on the point of bearing fruit. In particular;

1. Celanese Corporation, working purely on company funds, has built up a capability to produce excellent clean ceramic powders which when combined with a suitable polymer yield composites with $d_h g_h$ figure of merit up to $5,000 \ 10^{-15} \ m^2/V$, a factor of two better than the best PVF2. That this is not yet even the optimum is evidenced by recent 0:3 polymer: ceramic composites from NGK in Japan which have a $d_h g_h$ product better than $10,000 \ 10^{-15} \ m^2/V$.

2. Cyanamide Corporation has over the last six months produced a flexible ceramic PZT fiber. They have demonstrated that it is possible to make a PZT cloth by

conventional textile techniques using this fiber and with an impregnation using a suitable elastomer, a highly flexible piezoelectric composite can be produced.

This development is the critical key which was necessary to open the possibility for large area samples with fine internal microstructure, which could exploit the full connectivity control of tensor properties which the composite affords. Cyanamide sees no special difficulty in using the fiber in a full three dimensional weave.

Both these promising company developments have been carried forward, so far, on purely internal funds. They look most attractive for large area systems, but if they are to continue much longer there must be the indication of strong DoD interest and potential support. I believe it would be a real setback to the future program if these commercial ventures were to flounder at this stage.

In transducers current research in adequately funded and is progressing well. For sound absorbers, I believe there is urgent need for expanded research and the exploration of completely new approaches. The old dashpot spring type damping looks difficult if not impossible to fully implement in systems which must stand deep submergence. What about other possible mechanisms - e.g., magnetic systems using eddy current damping? Piezoelectric systems using electric resistivity damping. Ferrofluids in conducting tubes, etc..... It is not just new research on the old tired systems, which is certainly required, but some "idiot funds" for revolutionary new thinking which might find totally new ways out of the current "box".

US ELECTRONIC MATERIALS COMPETITIVENESS:
The Crisis and Proposed Resolutions

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ECONOMIC AND NATIONAL SECURITY

Since 1980 US competitiveness in a number of high-technology areas including microelectronics and, in particular, electronic materials has been declining. One of this country's leading competitors, Japan, has assessed its own advanced technology position in semiconductors as being highly competitive and on a lasting basis[1]. At present, Japan commands 70% of the world market in 64K RAMS, and 95% of VCR's and compact disks[2]. Moreover, Japan has overtaken the US in optoelectronics and it is catching up rapidly in the field of biotechnology[3].

How will the US fare in other technological areas important to its security? In addition to advanced silicon these areas include the gallium arsenide technologies, electro-optic materials, ceramics for packaging high-speed electronic components, and nonlinear optical materials and components for optical computing and laser applications.

The present crisis has been nurtured not only by intense Japanese competitiveness but also by a degree of complacency in the nation's high technology sector. Our dominance of the 50's is being accepted somewhat unrealistically as the status quo. The prevalent "NIH (Not Invented Here) Syndrome" tends to waste valuable innovative resources in its insistence on reinventing foreign technologies[4.] The US has, with great generosity, given access to its technology to other countries at cheap prices. For example, the technology transfer from the US and Europe to Japan in the period 1951-1983 has cost Japan about $17 billion through licensing and other agreements. This amount expended over 30 years to provide the underpinnings for Japan's entire

high technology development, is almost the same as the $18 billion spend by the top twenty US corporations in 1983 *alone* for R&D activities[5].

This crisis affects not only the economic well-being of this country but also its national security. Currently, US defense capability relies in large part on a superior electronic technology involving, for example, major components such as sensitive infrared sensors and numerous subsystem components such as ultradense silicon circuits. Japan has recently taken the lead in commercial production in both areas cited in these examples. Thus, the US is increasingly moving toward dependence on off-shore suppliers for many essential components in its most advanced weapons and commercial systems. In the near future, this situation is likely to place the US at the mercy of foreign vendors. Since the design of advanced systems must be based on an understanding at the manufacturing level of the most sophisticated components, this reliance may limit the capability to innovate the required electronics hardware. In effect, a foreign monopoly in critical materials technology may well cost the US its edge in advanced electronics.

National security, in its broadest sense, must include international trade. US-discovered commercial technologies that are permitted to develop abroad at a faster pace can lead to US dependency on a potential monopoly that is inimical to national interests. Particularly relevant here is the fabrication of electronic materials having the degree of purity and perfection required by present-day technological requirements. Such materials have an enormous added value when they are used to make components and subsequently systems. The size of the market for Si wafers was $3.4 billion in 1984. The Si-IC market involving components was $34 billion during that same year. Their use in computers amounted to an annual market of hundreds of billions of dollars[6]. The implications of such leverage are enormous for both commercial and defense sectors.

THE JAPANESE APPROACH

Japan has viewed itself as a technology-based nation since 1980. That year has been dubbed "The first year of the era of Japan's technological independence" by the Minister of Japan's Science and Technology Agency[7]. This view is substantiated by the increase for electronics R&D which has been estimated by the Electrical Industry Association of Japan as 26% per year between 1978 and 1982[8]. The startling surge of patents issued to Japanese companies confirms impressions about a possible shift of the world locus of innovation to Japan and ultimately to the Far East in general[9].

The Japanese methodology for achieving economic dominance contains two principal ingredients: an unremitting quest for market control undergirded by a strong growth bias, and the use of available capacity designed for an expanding market even at the risk of a short term financial loss. Large capacity is necessary if the learning curve for manufacturing a high technology product is to be climbed rapidly. Thus, the Japanese investment level in a promising technology is stepped up when demand is weak rather than being curtailed. In 1976, for example, the US cut back on the production of RAMS during a recessionary period. Japan, by contrast, pressed on despite temporary financial losses to take a lead in the production of 16K and 64K RAMS which the US has since been unable to surpass[10]. A recently added new ingredient involves a strongly increasing emphasis on R&D. As a percent of sales in 1983, R&D amounted to 3.4% and 6.6% for GE and TI, respectively. For the corresponding Japanese companies, Hitachi and NEC, the percentages were 7.9 and 13.0, larger by a factor of two (although smaller in terms of absolute amounts)[11]. These differences should be viewed in a broader time frame. During the twenty year period preceding 1984, the total R&D expenditures as a percentage of GNP *increased* by about 50% for Japan and *decreased* by more than 10% for the US[12].

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US-UNIQUE CAPABILITIES

The US R&D infrastructure is still very powerful. "Yankee Ingenuity" persists and has brought about the strong industrial base in which this ingenuity can flourish. This base is coupled to strong leadership in all basic sciences. The nation enjoys the benefits of many distinguished universities which train excellent engineers and scientists, albeit not in sufficient quantities. (In 1982, the number of engineering graduates per 100,000 persons was 62 in Japan, and 29 in the US[13].) A strong sense of entrepreneurmanship, which is also part of the national image, is evidenced by the large number of successful venture capital initiatives.

DoD plays a strong role in funding and nurturing research while frequently engendering activities having spin-offs in the commercial sector. The VHSIC program, for example, was successful because it provided the computing industry with challenges and the financial means to meet them at the time when industries themselves were ready to attack the very same problems[14]. As a result, the time interval required to bring about the present VLSI capabilities was appreciably contracted. Defense science-driven research has brought about many commercially applicable advances in other areas as well. RSR (Rapid Solidification Rate)-produced alloys, for example, are already becoming a commercially significant outgrowth of DoD-sponsored research in metallurgy.

Continued development of this country's scientific and technological base depends on a number of factors. Among these are: (1) a long-range view towards funding policies in both the civilian and defense section; (2) a strengthening of the scientific educational base in universities; (3) an effort to increase interactions among industrial institutions; and (4) a more lenient interpretation of industrial activities that might be interpreted as having an antitrust component. Indeed, some encouragement of industrial cooperation can be provided by a DoD contractual umbrella.

NEED FOR SYMBIOTIC TECHNOLOGICAL ENTERPRISES

The needs for advanced technologies by both the defense and commercial sectors are inseparably intertwined. Technical strengths must therefore be coordinated to deal effectively with both economic and national security problems. One approach to coordination is institutional. Such an approach must provide a mechanism for industrial interchanges without abandoning long-term strengths. It must eliminate the mind-set that associated DoD-sponsored R&D solely with potential defense needs. Also it must preserve the spirit of technical creativity engendered in small-scale research settings which is prevalent in this country. Small-scale research activities at universities are a source of new ideas, insights, and new technical manpower. These are important in all commercial ventures for generating proprietary ideas that can be commercialized successfully.

The technological overview and insight provided the Japanese Ministry of International Trade and Industry (MITI) is not matched by any institution within the US government. MITI's closest counterpart in this country appears to be DARPA. The major role of MITI lies not in the sponsorship of research, but rather in planning, coordinating, making financial arrangements, and establishing industrial policy. Some research is sponsored at individual companies as a subsidy to stimulate growth and/or to accomplish specific goals. Subsidized projects have finite lifetimes in the range of 5-10 years. The bureaucracy is small. Ten officials supervise the major projects, with an average of one project per official. A notable feature is MITI's encouragement for symbiotic technological enterprise by way of institutional means. Japan's Opto-Electronic Joint Research Lab (OJRL) involves MITI and a number of participating industries including Fujitsu, Furukawa, Hitachi, Matsushita, Mitsubishi, NEC, and Toshiba. There are six research groups concerned with bulk crystal growth, maskless ion implantation, epitaxial growth, applied surface physics, fabrication technology, and

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characterization. The fifty or so researchers associated with OJRL work at a single site with a small support staff.

Some cooperative research organizations, for example, the Microelectornics and Computer Technology Corporation (MCC) and the Semiconductor Research Consortium, have also been formed in the US during the past few years. MCC, founded in January 1983, shares several of OJRL's characteristics. MCC is a purely industrial consortium consisting of 21 shareholders including Bell Communications Research, Boeing, Digital Equipment Corporation, Eastman Kodak, Honeywell, Lockheed, Martin Marietta, RCA (GE), Rockwell International, 3M, among others. Each shareholder pays $1 million per share in the corporation plus annual fees for each program in which it participates. All work is done on-site by about 340 research staff members. About a third of these are employees of shareholder companies. One of MCC's objectives is to maximize technology transfer to companies. The four major research areas are packaging, software, VLSI-CLAD, and advanced computer architecture. There is essentially no materials research component.

NATIONAL ELECTRONIC MATERIALS INSTITUTES

The US has been successful in creating novel institutional formats when needed in times of crisis. Notable examples are the formation of the National Laboratories during World War II to develop nuclear technology, Lincoln Labs to continue the development of radar into the postwar era, and the Jet Propulsion Lab to establish the US space capability. There is no current corresponding institutional arrangement for addressing the electronics material and fabrication crisis.

The National Electronic Materials Institutes (NEMI) proposed here are designed specifically to strengthen high technology areas such as optoelectronics, in which the US is lagging. The research management approach is novel and designed to meet

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existing technological needs by optimizing interactions among industries, the defense science establishment, and universities. An institute concerned with optoelectronics technology would recognize that while a strong US technology exists, its progress is impeded by broad dispersion and lack of coordination among groups addressing this field. It would also take cognizance of the extensive DoD and commercial applications of this area. In addition it would focus on the need to be competitive with a corresponding massive Japanese (second generation) national technology project to be capitalized at about $90 million for its first year, commending in June, 1986[15].

Several such institutes might be visualized, each emphasizing a different important technological objective. Bulk and layered crystal growth and scientific instrumentation development, for example, are currently receiving disproportionately low R&D support and would benefit from focused technological efforts of the kind to be described.

Each institute would be located in a carefully chosen geographical area containing a mix of high technology industries and universities strong in both physical and engineering sciences. Such a location would provide a rich source of the required talented manpower. The institutes would deal with topics directly related to electronic materials, processing and devices in a broad multi-disciplinary and multi-institutional manner. They would be based on strong industrial participation through the presence of creative scientists spending limited periods of perhaps three years on loan (or on partial loan) from their parent institutions. This period of close association would be followed by continued interaction on a more informal basis.

The institutes would benefit further from the participation of faculty members and their graduate students on a continuing basis, thereby assuring that innovative research using state-of-the-art equipment is carried out within a goal-oriented atmosphere and

that your scientists are adequately trained to move into positions of technological leadership.

Activities would range from targeted fundamental exploration to prototyping (to prove reliability and reproducibility of components) but not systems. Proprietary exploitation and scale-up to automated, efficient, cheap, reliable, and high-yield production would be left to industry which could range from small-scale manufacturers to larger establishments. The success of commercialization efforts clearly depends on the effectiveness of bringing about technology transfer between the institute(s) and the commercial establishments. Problems of technology transfer impose enormous difficulties within large companies concerned with moving a potential product from the research laboratory to an operating component. The problems in the case of a NEMI will also be challenging.

An important ingredient of technology transfer would utilize the through-flow of scientists (industrial visitors, graduate students, and post docs) to disseminate acquired expertise.

Funding needs to be both stable and sufficient to guarantee state-of-the-art facilities for materials fabrication and characterization. These facilities should be equal to the best available in any of the major US electronics industries. For a given institute, capital equipment costs to acquire instrumentation may be in excess of $30 million for the first year. Appreciable amounts are required in succeeding years to maintain state-of-the-art capability. The annual budget for one institute might be of the order of $25 million. Major start-up funds are to be supplied by DoD. With time, participating industries become the principal funding source for a given project area.

For a given R&D area, DoD funding generally terminates after 5 to 10 years. Subsequently, the institute or the affected institute division is either supported by one or more industrial establishments, or is disbanded.

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The institutes are to be managed independently of the participating institutions, but the board of directors, containing representatives of these institutions including members of DoD, would set or approve research directions. Their composition mandates location in a large, easily accessible metropolitan area such as Los Angeles, San Francisco, Chicago, Boston, or New York.

Patents, although owned by the NEMI, would be available to participating industries and others under suitable licensing arrangements. It is intended that DoD enjoy a royalty-free license for the utilization of any inventions for its own purposes. It is hoped that means could be found to encourage commercial development of new electronic devices or systems through tax incentives.

These institutes are not intended to replace any of the presently used mechanisms for furthering nationally important R&D. Rather, they will serve the crucial function to integrate the highly productive but practically diverse national research output into industrially useful packages.

The US could afford to create three or four institutes devoted to electronic materials-related problems at a cost no greater than that of the Strategic Computing Initiative. A conservative approach towards exploring the utility of this institutional framework involves the initial formation of one institute addressing opto-electronic technology. At the same time, an impending crisis of competitiveness in fields other than electronic materials, that may not yet be recognized, must be viewed as a genuine possibility for the future. The institutional format described here may therefore have wider utility.

It must be emphasized that the establishment of such an institute represents a high-risk experiment, but an experiment having a potentially high payoff. The country cannot afford to be noncompetitive in the field of electronic materials which provides the underpinnings of its entire electronic technology. The same is true for the computer

industry. Appropriate steps have been taken to help remedy the situation in the latter case by means of the Strategic Computing Initiative. We can afford to do no less for electronic materials[16].

ACKNOWLEDGEMENTS

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OPPORTUNITIES IN MATERIALS CHEMISTRY

J. L. Margrave

In order to meet the many sophisticated challenges of our high-technology, it is more and more the fact that new materials must be "designed" for the application. Thus, to find a refractory, oxidation-resistant material with a low thermal expansion coefficient that can be machined or formed by some other technique into a shape within small tolerances requires the synergistic interaction of physics, chemistry and materials/engineering. In this discussion, special attention will be directed to those areas which involve chemistry, but always in support of the multidisciplinary materials goal.

Goals Of Chemistry

Without expecting to provide a set which satisfies every chemist, one can still identify some basic goals:

(1) The synthesis, purification and characterization of materials.

(2) The understanding of natural phenomena on an atomic/molecular scale.

(3) The improvement of processes and properties.

(4) The prediction of new phenomena.

(5) The synthesis of new materials to meet the needs of modern technology.

In other words, chemistry offers the opportunity to obtain "designer" species, synthesized to meet the requirements of the materials scientist/engineer. In order to achieve this, chemists make use of the variation of properties under extreme conditions: high/low temperatures, high/low pressures, high/low reactivity, high/low impurity levels, high/low gravitational fields, etc.. In most of these cases, one can now cover ranges of 10^{15} - 10^{20} in the variable being used and thus can provide the basis for optimizing materials properties.

As an example, impurities at the ppm-level can completely degrade the properties of electronic materials like Si or GaAs. Even at the ppb-level, impurities may lead to ambiguous, non-reproducible experiments, unpredicted failures and mis-interpretation of theory. A complete chemical characterization is fundamental to the development of applications for new materials.

Experimental Opportunities

In addition to the designer-approach to materials synthesis, based on carefully documented properties/parameters/structures, there is a less predictable but potentially more exciting type of materials synthesis -- the exploration of truly new chemical reactions. Four such new opportunities in materials chemistry are:
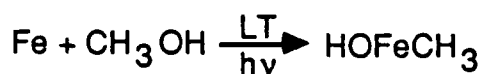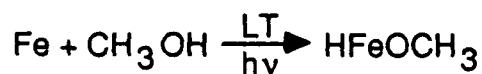
(1) The preparation/reactions of clusters generated by laser-irradiation of solids.[1,2,3] For example,

$$C(\text{Graphite}) \xrightarrow[\substack{\text{Nd-YAG} \\ \text{or} \\ CO_2\text{-Lasers}}]{h\nu} \underbrace{C_1, C_2, C_3, C_4, \cdots}_{\substack{\text{Reactive} \\ \text{Species}}} \underset{\substack{\uparrow \\ \text{A Spherical Cage} \\ \text{Molecule--A New} \\ \text{Polymorph of Carbon}}}{C_{60}} \cdots C_{100} \cdots$$
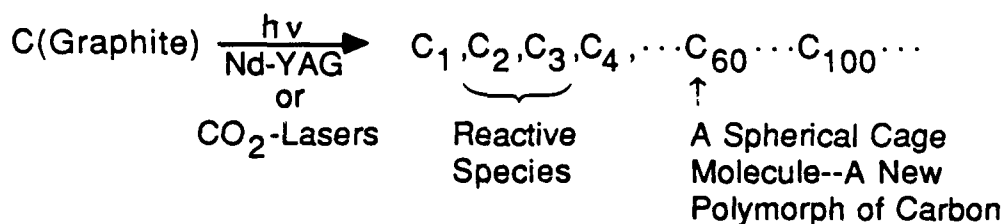
The species C_1, C_2, and C_3 can be reacted with H_2, O_2, N_2, CO and H_2O to form species like CNN, C_2O, C_3O, C_4O, C_2H_2 and $HC \equiv C\text{-CHO}$.[3] C_{60}^+ ions have been detected mass-spectrometrically from graphite sublimation gases[1] and $C_{60}La^+$ has been reported from laser-irradiation of La-doped graphite.[4]

Laser-sublimation of Fe, Co, and Ni yields clusters, M_x, where X = 1-100 or more.[5,6] Some reactions with H_2, O_2, and H_2O have been reported, but the products are poorly characterized.

(2) The low temperature synthesis of new organo-metallics by direct insertion of metal atoms/clusters into C-H, C-O, C-C, O-H, N-H or F-H bonds. This type of reaction has been explored for iron atoms[7-13] as shown below:

$$Fe + H_2O \xrightarrow[h\nu]{LT} HFeOH$$

$$Fe + CH_4 \xrightarrow[h\nu]{LT} HFeCH_3$$

$$Fe + \Delta \xrightarrow{LT} \boxed{\quad}\!-Fe$$

$$Fe + CH_2N_2 \xrightarrow{LT} FeCH_2 + N_2$$

$$Fe + C_2H_4 \xrightarrow[h\nu]{LT} HFeC_2H_3$$

$$Fe + C_2H_2 \xrightarrow[h\nu]{LT} HFeC_2H$$

$$Fe + CH_3OH \xrightarrow[h\nu]{LT} HFeOCH_3$$

$$Fe + CH_3OH \xrightarrow[h\nu]{LT} HOFeCH_3$$
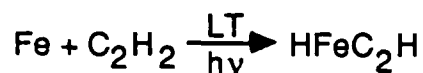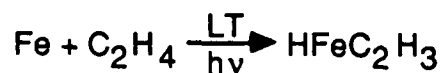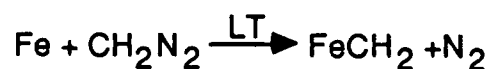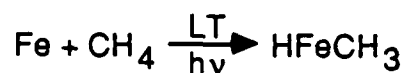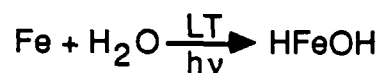
Another interesting example:[14,15]

$$Si + H_2O \xrightarrow{LT} HSiOH \text{ (cis- and trans)}$$

$$\xrightarrow{LT} H_2Si = 0$$

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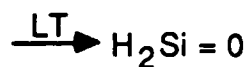
Finally, Li atoms react with CO as follows:[16]

$$2Li + 2CO \xrightarrow{\text{LT}} Li_2C_2O_2 \quad \text{, an ionic solid}$$

$$[2Li^+; \; {}^-OC \equiv CO^-]$$
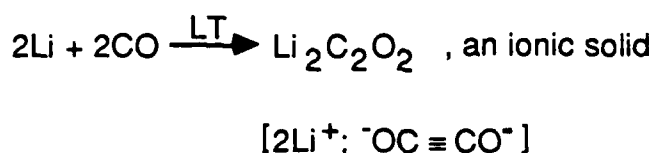
Thus, an active metal (Li, Na, K . . .) + CO reacts via electron-transfer to form a CO-dimer ion with a triple bond, and yields the dimetal salt of dihydroxyacetylene.

These reactions of high-temperature species (metal atoms/clusters) with low-temperature species (typical organic molecules) can be efficiently carried out on cold surfaces (LN_2 or liquid He-cooled). Literally thousands of new organo-metallics can now be synthesized and these will find use as ceramic/ceramic fiber precursors, for MOCVD applications, as synthetic intermediates, in thin film technology, etc.

(3) Pressures in the megabar range can now be routinely generated in the laboratory with the diamond-anvil cell and the compressed samples can be laser heated.[19] The formation of new diamond analogs (BCN, AlBN, B_2O, etc.) and of new oxides/halides like FeO_2, FeO_3, FeF_4, FeF_6, etc. should be possible[18]. The properties/uses for such materials are only guesses.

A similar unique opportunity for a scientific breakthrough lies in the area of ultra-high-pressure organic chemistry. Literally nothing is known about organic reactions at 50-100 kbars and beyond.[19] The area is ripe for exploitation.

(4) Very thin films and really clean surfaces have become available to chemistry/physics/materials science in the last decade and there are many opportunities for materials synthesis. For example, CVD of diamond[20] or cubic-Bn, MOVCD of metal oxides or metal carbides; fluoro-films for lubrication[21]; and alloy surfaces of arbitrary stoichimetries[22] represent only a few of the new types of surfaces which can be prepared.

Summary

Materials chemistry is an essential part of materials science and research planning for future materials developments should include significant commitments to the development of a complete chemical characterization. Structural details and a full understanding of the role of impurities can be of critical importance.

Finally, new materials concepts/syntheses represent the long term opportunities. As outlined in this note, the use of extreme conditions (low-temperature reactions of high-temperature species) and of special techniques (ultra-high pressures, MOVCD, fluoro-films, and ion-implantation) open up exciting new approaches to the design/preparation of materials for the future.

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21. See for example, U.S. Patent No. 3,758,450, Sept. 11, 1973, and various improvements, i.e., G. Tarancon, U.S. Patent No. 4,576,837, March 18, 1986.

22. For example, sputtering, ion implantation, plasma spraying or MOCVD could be used to form surface alloys.

DIRECT SYNTHESIS OF NEW
ORGANOMETALLIC COMPOUNDS

J. L. Margrave and Associates*

The preparation of new chemical compounds with direct metal-carbon bonds has been a goal of inorganic chemists since the discovery and characterization of ferrocene, $(\pi\text{-}C_5H_6)_2Fe$, in 1951.[1] The sandwich-type bonding in ferrocene and its analogs is unique and π-type complexes of transition metals with olefins, acetycenes, and allyls have been widely studied.[2] Although the direct formation of metal-carbon σ-bonds has been less extensively investigated, recent advances in metal atom/cluster chemistry have opened new doors for the direct synthesis of literally thousands of organo-metallic compounds.[3]

The technique which has been evolving for more than a decade utilizes the co-condensation of a high-temperature species (metal atoms/clusters) with a low-temperature species (organic molecules) on a surface cooled with liquid N_2 or liquid He. The high thermodynamic potential of the gaseous atoms or clusters may be sufficient to cause the reaction to go spontaneously or an additional boost to initiate reaction/may come from vis/uv irradiation. Overall, the reaction can be described as

$$M_x(g, condensed) + RH (condensed) \xrightarrow[hv]{LT} HM_xR \ (condensed)$$

In some cases an inert diluent may be needed but in liquid N_2 syntheses one simply uses an excess of the organic reactant. Most studies at liquid He temperatures use Ar or N_2 as diluents. Typical apparatus for gram-scale syntheses and for spectroscopic characterization of the reaction products (uv/vis/iv/Raman/esr) have been described in the literature.[4,5,6] Direct insertion reactions for metal atoms with H_2O, NH_3 and HF have been reported.[7,8,9]

Direct Insertion Into C-H Bonds

Earlier studies of metal atom interaction with H_2O, NH_3 and HF were extended to the isoelectronic analog, CH_4, in 1980[10,11] and it was shown that
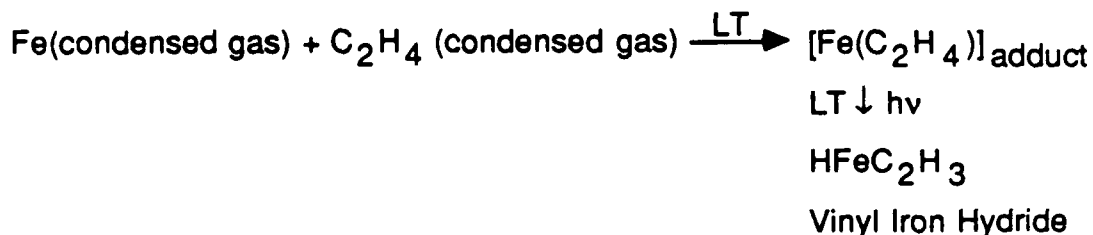
$$M \text{ (condensed gas)} + CH_4 \text{ (condensed gas)} \xrightarrow{\frac{\text{Liq. He}}{2}}$$

$$M(CH_4)_{\text{adduct}} \xrightarrow[\text{hv}]{\text{LT}} HMCH_3 \text{ (matrix)}$$
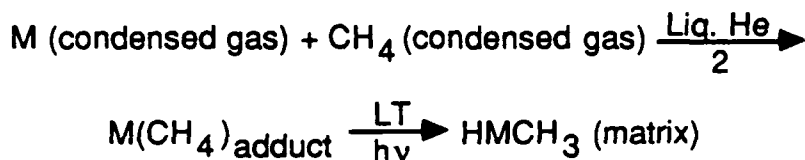
where M = Fe, Co, Ni, Cu, Ag, Au.[12] This reaction represents the first direct insertion of a metal atom into C-H bond. Extended studies of this reaction using other metals (Al) and other saturated hydrocarbons (C_2H_6, C_3H_8) have been published.[12,13]

Although transition metal compounds often interact with olefins and acetylenes to form π- complexes and with cyclopentadiene to form ferrocene-analogs (Fe, Cr, Ni, Co, Ti, W, etc.), the reactions of C_2H_2, C_2H_4, C_5H_6, etc. with metal atoms/clusters are only recently reported[14,15,16] The specific reactions vary from metal to metal. For example, Fe atoms interact with ethylene as follows:

$$Fe(\text{condensed gas}) + C_2H_4 \text{ (condensed gas)} \xrightarrow{\text{LT}} [Fe(C_2H_4)]_{\text{adduct}}$$

$$\text{LT} \downarrow \text{hv}$$

$$HFeC_2H_3$$

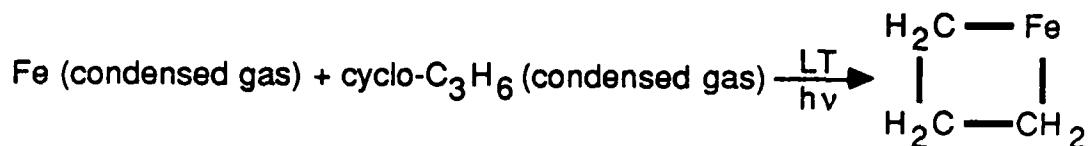Vinyl Iron Hydride

Co-atoms react similarly. Neither Fe_2 nor CO_2 insert into the C-H bond.

Fe-atoms interact with C_2H_2 to form $HFeC_2H$ (ethynyl iron hydride) and with cyclopantadiene to form $HFeC_5H_5$ (cyclopentadienyl iron hydride).
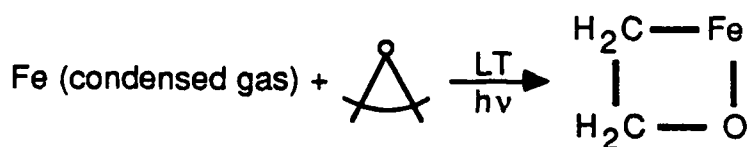
Nickel atoms form traditional π-complexes with ethylene but form a new organometallic with acetylene,[17] Ni = C = CH_2 (vinylidene nickel)

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Direct Insertion Into C-C Bonds

The direct insertion of Fe-atoms into the strained cyclopropane ring has been observed:[18]

$$Fe \text{ (condensed gas)} + cyclo\text{-}C_3H_6 \text{ (condensed gas)} \xrightarrow[hv]{LT}$$

$$\begin{array}{ccc} H_2C & \!\!\!\!-\!\!\!\! & Fe \\ | & & | \\ H_2C & \!\!\!\!-\!\!\!\! & CH_2 \end{array}$$

With ethylene oxide, one observes[19]

$$Fe \text{ (condensed gas)} + \triangle\!\!\!\!O \xrightarrow[hv]{LT}$$

$$\begin{array}{ccc} H_2C & \!\!\!\!-\!\!\!\! & Fe \\ | & & | \\ H_2C & \!\!\!\!-\!\!\!\! & O \end{array}$$

Attempts to react metal atoms with the highly strained cubane molecule have not been successful[20] but other strained ring systems are under investigation.

Direct Insertion Into O-H Bonds Of Alcohols

Interactions of Fe, Co and Ni atoms with methanol lead to O-H bond insertion.[21,22] For example:

$$Fe \text{ (condensed gas)} + CH_3OH \text{ (condensed gas)} \xrightarrow{LT} [Fe(CH_3OH)]_{adduct}$$

$$LT \downarrow hv$$

$$HFeOCH_3$$
methoxy iron hydride
and $HOFeCH_2$
methyl iron hydroxide
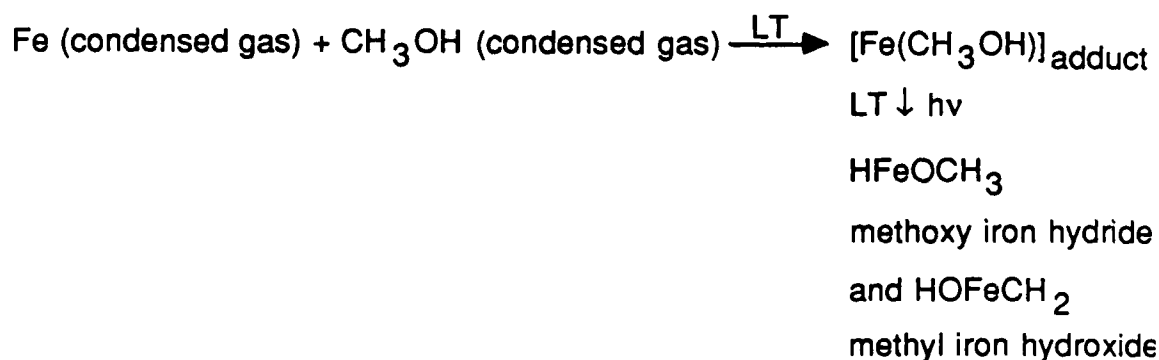
Co and Ni behave similarly. Further studies of ethanol, ethylene glycol and glycerol are in progress.

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Direct Insertion Into C-O Bonds of Alcohols And Ethers

Co-deposition of metal atoms with ethers leads to insertion into the C-O bond:[23]

$$M \text{ (condensed gas)} + ROR' \text{ (condensed gas)} \xrightarrow{\text{LT}} [M(ROR')]_{adduct}$$

$$LT \downarrow h\nu$$

$$\begin{pmatrix} RMOR' \\ ROMR' \end{pmatrix}$$
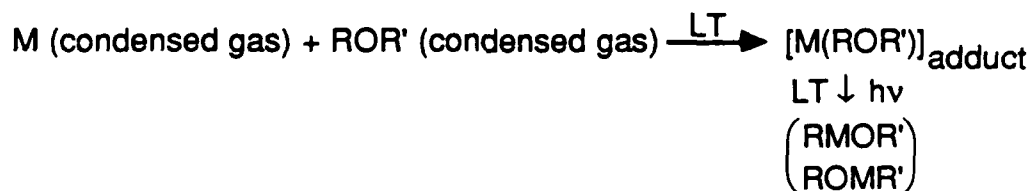
Thus, for Mn, Fe, Co and Ni interacting with dimethyl ether, we have prepared 0.5 gram samples of methyl-methoxy iron (CH_3-Fe-OCH_3) and the other metal analogs.

Direct Preparation Of Bare-Metal Carbenes

Recently we reported the first preparation of bare-metal carbenes by the following reaction:[24]

$$Fe \text{(condensed gas)} + CH_2N_2 \text{ (condensed gas)} \xrightarrow{\text{LT}} Fe = CH_2 + N_2$$

We have now extended this synthesis to several of the first-row transition metals.[25] Such metal carbene species are ideal precursors for "designer" organometallic systems. For example, one can add CO to get methylene iron carbonyls or add H_2 to get $HFeCH_3$. NH_3 should lead to NH_2 ligands, and CH_4 to dimethyl iron adducts. There are many possibilities and one has to conclude that organometallic syntheses from bare-metal carbenes are still in a primitive stage.

Activation of CO and CO_2

Slightly different approaches to organometallic synthesis are found in the activation of CO and CO_2 by metal atoms. Nearly 15 years ago we described the reactions of alkali metal atoms with CO.[26] For example:

$$2Li(\text{condensed gas}) + 2CO(\text{condensed gas}) \xrightarrow{\text{LT}} \left\{ \begin{array}{l} Li(CO)_2 \\ LiCO \\ Li_2(CO)_2 \end{array} \right\}$$

$$\text{LT} \downarrow$$

$$Li_2C_2O_2 \text{ (crystalline solid)}$$
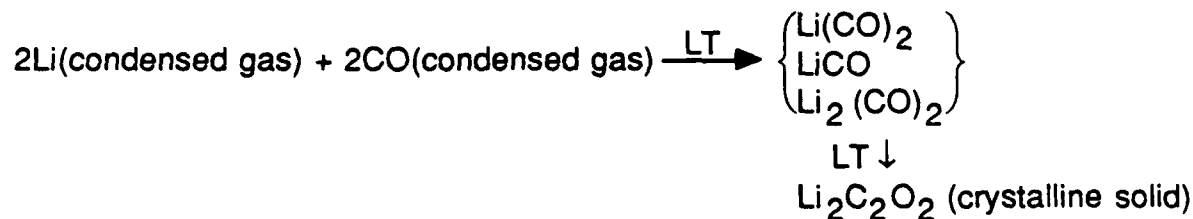
$Li_2C_2O_2$ is more clearly described by the picture

$$[Li^+, {}^-OC \equiv CO^-, Li^+]$$
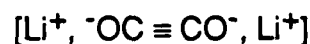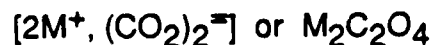
i.e., it is the dilithium salt of dihydroxy-acetylene. The other alkali metal analogues are also known.[27]

For Li, Na, K, Rb, and Cs plus CO_2, one observes[28,29] species like

$$[M^+, CO_2^-], [M^+, (CO_2)_2^-]$$

and, ultimately, the metal oxalate:

$$[2M^+, (CO_2)_2^=] \text{ or } M_2C_2O_4$$

Thus, the usually inert CO_2 had been activated to form a useful organic salt.

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Summary

The direct use of metal atoms and clusters for synthesis of organometallic compounds has been demonstrated and several new types of compounds have been reported:

(1) HMR   where $R = CH_3, C_3H_5, C_2H_3, C_2H, C_5H_5$, etc

                                             $M = Fe, Co, Cu$, etc.

(2) $M = C = CH_2$ where $M = Ni$

(3) ROMH   where $R = CH_3, C_2H_5 \cdots$

                                             $M = Mn, Fe, Co, Ni, \cdots$

(4) ROMR'   where $R = CH_3, C_2H_5 \cdots$

                                             $M = Mn, Fe, Co, Ni \cdots$

(5) RMOH   where $R = CH_3, C_2H_5 \cdots$

                                             $M = Fe, Co, Ni, \cdots$

(6) $M = CH_2$ where $M = Fe, Co, Ni, Cu \cdots$

(7) $M_x(CO)_y$ where M = alkali metal

                                             $x = 1, 2$

                                             $y = 1, 2$

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(8) $M_x(CO_2)_y$ where M = alkali metal

x = 1 or 2

y = 1 or 2

(9)
$$\begin{array}{c} H_2C - M \\ | \qquad | \\ H_2C - CH_2 \end{array}$$
where M = Fe, Co, Ni ···

Because of the generality of these reactions and the essentially unexplored potential for reaction of metal dimers, trimers and high clusters, one can safely predict that literally thousands of new organometallic compounds can be prepared. All we need are the "designer's specifications" to decide which M with which R in which type of compound will give a volatile species for MOCVD of an appropriate thin film or for growth of a unique crystal!

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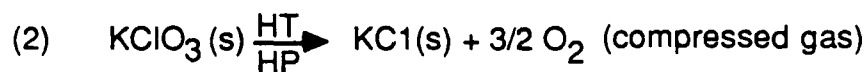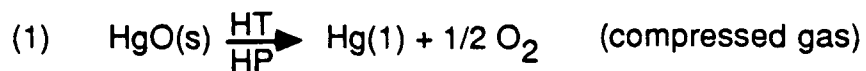
PREPARATION OF NEW OXIDES BY HIGH PRESSURE TECHNIQUES

John L. Margrave

The oxides of the elements are among our most common minerals, are the source of most of our metals and are among the most widely used materials in our society - building stones and cement, glass, gemstones, and quartz crystals for clocks and watches, for example. Natural oxides tend to be quite stable and often are high-melting. In the laboratory, one can expose metals (or oxides) to reducing or oxidizing environments which can result in intermediate states of oxidation (sub-oxides) or to other states of oxidation (peroxides, superoxides, etc.) During vaporization or decomposition at ambient pressures, or lower, it is usual to find normal oxides losing oxygen to form sub-oxides[1], e.g., $SiO_2 \rightarrow SiO + 1/2\ O_2$. One can also form sub-oxides by the use of a reducing container[2], e.g., $B_2O_3 + C \rightarrow B_2O_2 + CO$.

Higher oxidation states are not always accessible for metals but may be for non-metals. Thus, in Na_2O_2 the oxidation state of Na is +1, but the oxidation state of O_2 is -1 rather than -2 as in Na_2O. In NaO_2 the oxidation state of Na is still +1 but oxygen is now -1/2. In NaO_3, the oxidation state of oxygen is -1/3. This situation is typical of oxides from groups I, II, and III of the Periodic Table, although not all of the possible peroxides, superoxides and ozonides are known. Very little work on peroxides, superoxides and ozonides of group IV or transition elements has been reported.

Typical syntheses of peroxides and superoxides make use of high O_2 pressures and/or high temperatures.[3] This poses experimental problems in that gas-tight, non-reactive containers at 500-1000° C and 50,000-100,000 psi are almost non-existent. Further, oxygen pressures over 20,000 psi are hard to achieve, even with intensifiers. Several years ago we described a technique for generating O_2, in situ, at pressures over 50,000 atm for synthetic purposes.[4,5] Thus,

$$(1) \quad HgO(s) \xrightarrow[HP]{HT} Hg(l) + 1/2\,O_2 \quad \text{(compressed gas)}$$

$$(2) \quad KClO_3\,(s) \xrightarrow[HP]{HT} KCl(s) + 3/2\,O_2 \quad \text{(compressed gas)}$$

If an oxidizable material is present, it will react. We reported the preparation of yellow, paramagnetic solids with the approximate stoichiometries BO_2, AlO_2 and GaO_2. Also, this technique was used for direct high-pressure oxidation of Cr_2O_3 to form CrO_2.[5] Although BO_2, AlO_2 and GaO_2 are probably examples of altered oxidation states of oxygen, the CrO_2 crystal contains an altered Cr-oxidation state and even the +6 state in CrO_3 is known.

It is the purpose of this note to outline synthetic approaches which should result in a variety of new oxides - especially new transition metal oxides. Thus one could take FeO or Fe_2O_3 and oxidize them at high pressures with HgO or $KClO_3$. Little is currently known about the hypothetical species FeO_2 or FeO_3 which could result. Are they "normal" oxides with super-valent metal or "normal" valent metals with sub-valent oxygen? In either case, these should be important new materials to prepare and characterize.

Similarly, one can seek to oxidize MnO or MnO_2, CoO, NiO or CuO to form MO_2, MO_3 and MO_4 solids. Also, the R_2O_3 - rare earth oxides would be suitable for high-pressure oxidation to RO_2 or RO_3 - solids. High pressure oxidations could also be used to attempt the preparations of SiO_3, GeO_3, SnO_3 and PbO_3. In the Group IV elements it is allowable to have six-coordinate ions ($SiF_6 =$, $GeF_6 =$, etc.) so trioxides appear possible. Either the monoxides/the dioxides/ serve as starting materials.

Initially, it will be practical to use either a moderately heated diamond-anvil cell[6] or a heated cell with cubic-zirconia anvils.[7] Detection of products should be feasible with either vis/uv or infrared spectroscopy through the cell while at high-pressures/high

temperatures. One hopes that the high-pressure phases will not revert when the pressure/temperatures are released so that samples can be conveniently studied and utilized. Laser heating through the transparent anvils is quite feasible. Larger scale syntheses could be performed with opposed anvil or tetrahedral anvil high-pressure device.

SUMMARY

By using oxygen-source compounds (HgO or $KClO_3$) confined at high temperatures in a high pressure cell, one can generate new oxides. Transition metal oxides like FeO_2, NiO_2, or RO_2 and RO_3 where R is a rare-earth metal could have interesting magnetic properties. SiO_3, GeO_3, SnO_3 and PbO_3 are probable stable species at high pressures.

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QUESTIONS FOR THE MATERIALS RESEARCH COUNCIL

1. From the viewpoint of fundamental materials science, could a combination of organic polymeric materials and superlattice structures be expected to build on the advantages of both as nonlinear optical materials to produce materials that are more nonlinear than either category by itself? That is, should DARPA pursue investigations of organic superlattices in the quest for better nonlinear optical materials? (John Neff)

2. Are bipolar devices possible in superlattices, i.e., can n and p type superlattices be combined to do something useful? (Sven Roosild)

3. Is it now possible to predict the nucleation, growth, and relative stabilities of "metastable" phases, their crystal structures and potential properties via computational means? If so, are we to a point where new technologically interesting materials (e.g., metastable phases of transition metal alloys) could be addressed by "computational metallurgy"? (Phil Parrish)

4. One crying need in visible eye protection is fast photochromic materials that can switch from transparent (clear, uncolored) to highly absorbing (OD > 3) in the μsec time frame. What types of molecules should be pursued that can meet these requirements? What general principles should one exploit? Is it more appropriate to investigate organic than inorganic systems because of the flexibility in molecular design in the former? (Joe Friebele)

5. I propose the MRC consider the application of high-temperature composites to high performance gas turbine engines. Topical areas such as carbon-carbon and ceramic composites have received attention in past MRC sessions, and it would now be helpful to obtain their opinion on how we direct our materials development toward the preeminent hot turbine application. It seems to me that an emerging need is to provide a testing capability which explores the multi-dimensional characteristics of these materials under realistic (temperature/pressure) conditions. (Frank Patten)

6. In what areas of Material Science does the Council think the advances in computational chemistry will be useful and when might one see it applied? As a corollary question, what areas of computational chemistry (if any) should be pushed for the benefit of material science. The Council should have access by next July to at least a draft of an IDA study stating their views. (Steve Wax)

7. We get enquiries (ideas?) 2-3 times per year concerning high pressure research. Are there any useful scientific or technological avenues to pursue in this field - other than making diamonds? (Ben Wilcox)

8. In spite of many years of research on ceramic armors, the basic mechanics of how a ceramic fails under penetration and, conversely, how it defeats a penetrator are unknown. Why is this the case, and what should be the structure of research to address this issue? What are the limiting technologies - experimental methods, knowledge of microstructural response, dynamic mechanics or ?? (Gene Farnum)

9. There appears to be a greatly increasing importance of chemistry in the field of materials research, both in structural and electronic materials. Should DARPA consider creating a Materials Chemistry Program? If the answer is yes, what should be the technical emphasis, and what would be the expected impact on DoD? (Ben Wilcox, Dick Reynolds)

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Response to Question #1: Would Superlattice Structures Having Organic and Semiconductor Components Have Advantages Over Either Component Alone As Non-linear Optical Materials?

G. M. Whitesides, D. K. Ferry, M. S. Wrighton, R. M. Osgood, J. K. Stille

The desirable qualities of semiconductor materials for non-linear optical devices are their robustness (mechanical and thermal stability), their compatibility with processes for semiconductor device manufacture, and the (relative) ease with which they can be obtained in high optical quality. The desirable qualities of organic materials are, in principle, very large dipole moments and polarizabilities (and hence high optical constants and efficiencies), low cost, and inexpensive processability using the techniques of polymer technology. An important and still unresolved issue is that of the relative sensitivities to damage by radiation of these two classes of materials. Organic materials have a tendency to degrade on illumination by processes such as photo-rearrangement and photo-oxidation, but crystals of organics may actually be more resistant to fracturing and microcrack formation on exposure to intense pulses of light than semiconductors, perhaps because organic solids are usually more readily deformed plastically than semiconductors, and because they may spontaneously heal mircocracks.

The conclusions of this discussion were:

1. A strong intuition that in principle materials based on combinations of organics and inorganics and/or metals could have desirable non-linear optical properties not found in either.

One type of system that would seem attractive is the multilayer structure sketched in 1:

1

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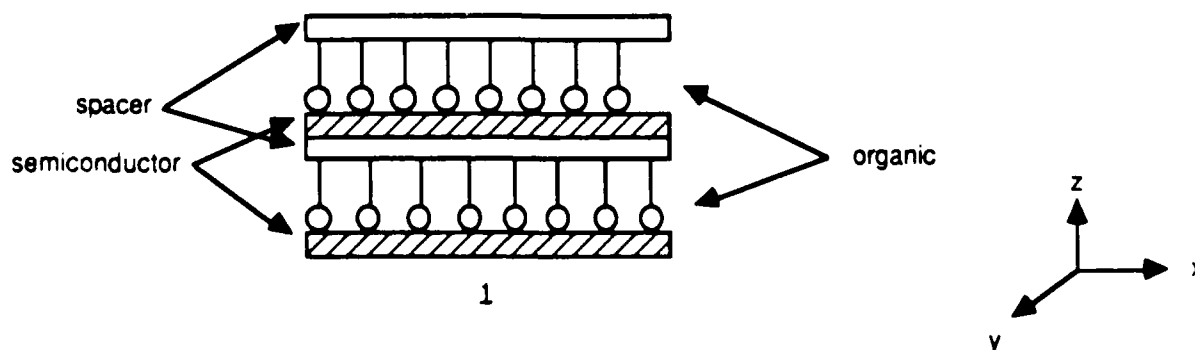
The semiconductor (or metallic/metalloid) film would provide high in-plane (x,y) polarizability. The organic layer would provide high polarizability in the z direction, and controllable anisotropy in the x,y plane (a characteristic that will be difficult to design into inorganic thin films). The spacer layer in this type of structure would be necessary to avoid an effectively centrosymmetric structure. An obvious concern is whether the growth conditions needed for the semiconductor layers would be compatible with the organic materials: thermally stable optically functional materials are required for the construction of multilayer devices of this type.

A second attractive system would use the so-called hyper-Raman effect now believed to be commonly observed in stimulated Raman emission spectroscopy at interfaces. The basis for this technique is fundamentally a semi-controlled superlattice technology: organic molecules adsorb on small metallic particles or surface projections having (presently) uncontrolled geometry. These particles respond to the electromagnetic field of the incident light, or to an applied electrostatic field, by amplifying it locally. The high local fields can, in some instances, strongly enhance the intensity of Raman emission by mechanisms that are still incompletely understood. Normal Raman uses exciting light of frequency, ω, and observes Raman emission at $\omega \pm \delta$, where δ is a vibrational frequency of the adsorbed organic. Hyper-Raman uses exciting light at frequency ω, and observes Raman emission at $2\omega \pm \delta$. The intensity of this frequency-doubled stimulated emission is much higher than anticipated (it may, for example, be of the same order of intensity as the normal Raman emission). The limitations to the efficiency of this process are not presently known.

2. A belief that although these leads and general arguments concerning anisotropy and polarizability support the proposition that combinations of organic and (semi)conductor structures might have attractive non-linear optical properties, the rational design of such systems will require a substantial amount of information that is not currently available.

• What is the relation between the structure (molecular, electronic, and ordered array/solid state) of organic materials and their non-linear optical properties in the absence of a (semi)conductor component? Although organic (and organometallic) molecules offer enormous flexibility in terms of

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potential structural variability, this flexibility cannot presently be used to good advantage because the fundamental structural features required for particular non-linear effects are not well understood.

• How do organic/organometallic materials interact with semiconductors and metals electronically? It is known that coordination of fluorescent organic materials to metal surfaces often (always?) quenches fluorescence by energy transfer. This observation is encouraging, in the sense that it implies strong coupling between the electronic states of the organic and the metal. It also indicates, however, that the electronic structure of the organic, and the lifetime of organic excited states, will be strongly influenced by the proximity of metals, and presumably by semiconductors as well. The strength of this interaction can certainly be controlled: by spacing the organic chromophore closer to or farther from the supporting metal/semiconductor interface; by changing the electronic structure of this support (from metals through semiconductors to low dielectric constant insulators); by imposing electrical or magnetic fields; perhaps by controlling the morphology of the interface.

Little background information concerning the electronic interactions between metals/semiconductors and adsorbed organics is presently available, and there is now no way of predicting the influence of these interactions on the optical properties of either the organic or the semiconductor chromophore.

• How does one build the assemblies that might be required to test or manufacture organic/semiconductor superlattice structures for non-linear optical effects? Self-assembled monolayer or Langmuir-Blodgett techniques will doubtless prove applicable to making test systems, and a relatively modest background is already available concerning the assembly of such systems when optical properties are the issue of interest. Self-assembly, in particular, would need to be more extensively developed using optically relevant semiconductors as adsorbing surfaces, and the capacity of appropriate, optically responsive organic chromophores (for example, structures such as 2) to form mono- and multilayers should be explored.

$$\underline{2}$$
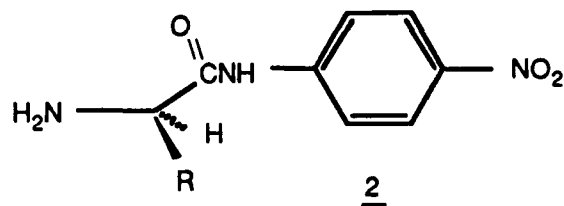
More complex systems (self-assembling ordered colloids, phase-separated polymers consisting of an optical phase and a transparent host phase, sol-gel-derived aluminosilicate structures) also provide promising targets.

SUMMARY

Semi-intuitive arguments based on considerations of polarizability and anisotropy suggest that combinations of organic/organometallic structures and semiconductor/thin film metallic structures should show strong non-linear optical responses. There is not presently enough experimental precedent or fundamental understanding of the relation between structure and optical response to predict the non-linear optical properties of pure components, much less those of composite structures. New techniques will be required to fabricate structures of these kinds.

Response to Question #2: Bipolar Superlattices

D. K. Ferry, M. Dresselhaus, R. Osgood, M. S. Wrighton

Bipolar structures can be made relatively easily in either heterojunction or superlattice form. Early examples of the former are the quantum-well lasers, the heterojunction bipolar transistors, and the high-electron mobility transistor. The sharp, precise control of dopant concentration and location allows one to transition from n-type to p-type layer within a few nanometers, as has been demonstrated in planar-doped barriers, hot electron transistors, and nipi superlattices.

Device applications for bipolar superlattices must rely upon the anisotropic nature of transport in the superlattice as well as the band-gap control. Transport normal to the superlattice is generally slower, or proceeds by successive tunneling. On the other hand, transport parallel to the layers may be enhanced by modulation doping. Thus, we expect the optimum devices to be those in which carrier transport is parallel to the layers.

Current nipi structures are homojunctions in e.g., either Si or GaAs. Superlattices based on nipi structures are unique in their absence of band offset phenomena. These devices are useful for a variety of optical devices including tunable detectors, and for nonlinear optical elements such as saturable absorbers. On the other hand, they could be fabricated from superlattices as well in which each doped region is a superlattice in its own right. This would allow one to use the superlattice structure for selection of wavelength sensitivity and refractive index effects. Tunable emitters should also be possible.

Use of the superlattice in a solar cell would confine the optically generated carriers by reducing diffusion (perpendicular to the layers). In addition, enhanced open-circuit voltages should be achievable because of the quantum well structure. This should also be true in stacked cell structures, and the heteroepitaxy may in fact make this technology more viable.

Response to Question #3: Are We to a Point Where New Technologically Interesting Materials
Could Be Addressed by "Computational Metallurgy"?

J. C. Williams

There are two methods for calculating the energies of constituents given their composition
and crystal structure. One of these is the thermodynamic method popularized by Kaufman and practiced
by many others (e.g., Chang, Watson and Bennett). The other is the total energy calculations as is being
done by Cohen at U.C. Berkeley and others. The former has the advantage of being able to evaluate the
relative energy of competing structures as a function of temperature and thus can help assess the
kinetics of decomposition reactions. The latter requires no experimental input data such as ΔH_o which is
a distinct advantage for new compounds and for systems which have not been previously studied
experimentally.

The methods of thermodynamics and kinetics (e.g., as discussed by Perepezko) have been
able to account for the existence of metastable phases observed in rapidly solidified phases. However,
ab initio physics or chemistry calculations to predict the occurrence of these phases have not yet been
successful. This is in part because the currently efficient computational methods permit comparison of
the energies of the various phases. These calculations requires a structure to be input which then allows
the ground state (0 K) energy to be calculated relative to that of the other phases which also have been
included in the calculation. The pathway to achieve these structures is not considered in these
calculations since they do not deal with the energy at temperatures above 0 K. It would appear that the
groups involved in the total energy (physics) calculations and those doing the thermodynamic/kinetic
calculations do communicate well with each other. Yet it may be productive to use the total energy
approach to calculate ΔH_o values to be used in the thermodynamic/kinetic calculations. Thus the
thermodynamic/kinetic approach and the total energy approach may have complementary value.

It is important to emphasize that while the predictive capability is not yet available, these
methods, in combination, allow the relative stability of relatively unstudied compounds to be estimated.
Such estimates should allow possible outcome of novel processing to be assessed. This has the

potential to guide the development of new, metastable materials but experimental studies are still necessary to follow up on the results of the calculations.

In summary it is clear that there is a need for improved coupling between the calculational and experimental approaches to materials science. The emergence of an productive confluence of these approaches can accelerate the development of new materials and can guide the experimental aspects of such efforts. DARPA can play an important role in catalyzing this outcome. To do this we recommend several specific activities as follows.

- Organize a workshop which brings the total energy calculation groups, the thermodynamic/ kinetic groups and the experimental groups to discuss materials development and their respective roles.

- Stimulate the initiation of an effort to calculate the ground state energy of a "catalogue" of transition metal compounds to be used as a complement to the catalogues of thermodynamic calculations compiled by Kauffman and the National Bureau of Standards group.

- Encourage the National Science Foundation to fund a limited number of studies to expand the theoretical framework for making these calculations beyond the current state which mainly uses pair potentials in a mean field approach. The goal of a better theoretical would be to develop some predictive capability.

Response to Question #4: Regarding Prospects for Approaches to Visible Eye Protection With Fast Photochromic Molecular Material

H. Ehrenreich, J. K. Stille, G. M. Whitesides, M. S. Wrighton

Photochromic materials are presently used in commercially available eyeglasses. Unfortunately, it is unlikely that simple photochromic materials will be useful for protection of the human eye and for protection of "electronic eyes" from intense optical flashes that cause blindness, because they are too slow, operate in the wrong spectral regime, or do not recover repidly enough. Photochromic glass presently used in eyeglasses absorbs in the ultraviolet (a small fraction of the solar spectrum) and darkens throughout the optical spectrum. Return to transparency is a thermal process:

$$\text{transport glass} \quad \xrightarrow{\text{UV light}} \quad \text{dark glass}$$
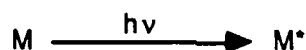$$\xleftarrow{\text{thermal process}}$$
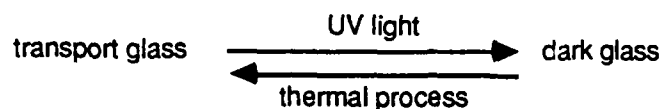
The overall system is relatively slow, especially recovery. However, molecular materials can lead to substantial improvement. UV-induced visible coloration, in principle, can be used to protect eyes and detectors from a flash that contains UV light and there are a variety of approaches that could be used that are fast (<10-6 s) and efficient (large optical density change per UV photon absorbed). Additionally, fast relaxation (<10-6 s) to the initial (transparent) state is possible. The following represent some molecular approaches to what might be termed "white flash" protection where the flash of light contains a broad spectral distribution that includes photons of sufficient energy to produce electronic excited states that give rise to absorption in a spectral region of interest:

> **EXCITED STATE ABSORPTION** - the high concentration of excited species produced by the leading edge of a white flash absorb at wavelengths where the ground state transmits. Excited states have unique optical properties compared to the ground state.

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EXCITED STATE PROTON TRANSFER - proton transfer can occur very rapidly upon photoexcitation of a molecular species and acid/base (pH) indicators establish that very large spectral changes can be induced by such simple chemistry. Excited states produced by the leading edge of the flash can undergo sufficient reaction to absorb the bulk of the remaining light in the flash.

EXCITED STATE ELECTRON TRANSFER - electron transfer is another fundamental excited state process that can occur rapidly and produces large optical absorption changes. Recent studies of linked donor-acceptor systems suggest promising systems for visible light protection systems.

EXCIPLEX FORMATION - like proton and electron transfer exciplex or excimer formation can occur rapidly and large spectral changes can be expected:

$$M \xrightarrow{ h\nu } M^*$$

$$M^* + M \rightarrow (M\text{-}M)^* \quad \text{(excimer)}$$

$$\textbf{or}$$

$$M^* + Q \rightarrow (M\text{-}Q)^* \quad \text{(exciplex)}$$

The excited state complexes $(M\text{-}M)^*$ or $(M\text{-}Q)^*$ can have unique absorption properties and like the systems described above can relax quickly.

The approaches described above do not appear viable for protection against monochromatic laser flashes at wavelengths longer than ~800 nm, because the molecular materials do not typically have electronic excited states that would be useful in achieving photochromic response. However, for broad spectrum or monochromatic flashes containing wavelengths shorter than 800 nm the approaches above, and others, can be considered viable.

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A key to improving molecule-based systems for optical flashes, in general, would be to develop molecular materials having unusual non-linear optical properties. This area is now under investigation in a large number of academic and industrial laboratories. Better specification of the materials requirements with respect to the flash protection problem should be provided to the research community, in order to assess whether the desired materials properties can be produced.

Response to Question #5: Hot Gas Turbine Materials (Carbon-Carbon Composites)

M. Dresselhaus, J. P. Hirth, J. L. Margrave

As an example material for hot gas turbines, carbon-carbon composites offer unique opportunities. Since the previous MRC meetings on the topic, there have been advances in understanding of the problems involved and some technological progress in solving them. The key issues are mechanically stable oxidation resistant coatings, control of oxygen interdiffusion and mechanical performance of the composite at high temperatures.

In view of this progress and in order to provide a basis for input by the MRC, we suggest that a one day session be devoted to carbon-carbon composites at the 1987 meeting of the MRC. The session could comprise one-third presentations by the development groups supported by DARPA (LTV, UTRC) and two thirds basic science issues and fundamental studies of coating material interactions and stability (Ir, HfC, etc.). The latter would include J. Margrave, G. St. Pierre and R. A. Rapp, who have addressed the specific problem of coatings for carbon-carbon composites. Differences in approaches for the T < 1500°C and 1500°C < T < 2200°C regions will be discussed.

Response to Question 6: Studies of Opportunities for Computational Chemistry

J. C. Williams

The presentation of the IDA Study of Opportunities for Computational Chemistry was not well received by the MRC and the final report is not yet available. While the study was timely and a good idea, the execution of the study by IDA, as judged by the presentation to the MRC, was unimaginative and seemed to focus more on the past and less on future opportunities, those which were identified in the study seemed pedestrian. As a result this question, as posed to the MRC, seems especially timely. The answer we provide is not intended to be a comprehensive exposition on opportunities in computational chemistries. Rather, we have attempted to identify a few areas where there is the potential for real progress and where such progress would complement the ongoing experimental effort in these areas.

Based on the July 25th session and subsequent discussions, there appear to be several areas where computational chemistry <u>can</u> be helpful to materials science. There are a couple of general points which bear on the specific recommendations. These are as follows:

- It seems important to select several sample problems which may allow the need for computations power to be bounded. Work on these problems would presumably also help identify the benefits of supercomputers to computational chemistry and identify the limitations (if any) posed by the current maximum computational power. In conjunction with this, estimates can be made of the future needs for computational capability. From this, federal funding agencies can begin to develop a capital investment strategy for university research that is responsive to the needs of the community and also is cost effective.

- The maximum payoff will probably be associated with attacking qualitative solutions to important problems rather than producing exact solutions to current computationally tractable problems.

Some of the problem areas which were identified as being important and for which important progress may be possible through application of computational methods include the following:

- <u>Surface and Interface Chemistry</u>: It appears that the extent to which other chemical species wet interfaces can be calculated using Monte Carlo methods. Such methods must account for the

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entropy changes associated with re-distribution, but this is tractable with more powerful computational methods and equipment.

- Optical Materials: There is a major advantage in using computational methods to calculate structure related optical properties. Such properties are important in connection with the application of organic compounds in non-linear optics.

- Phase Relations: The computational methods available for the calculation of phase relations in metals can now be applied to predict the occurrence of phase separation reactions in polymers. Here also, it is important to treat the entropic part of the problem so that ΔG is ultimately calculated rather than just ΔH.

- Reaction Control: Large scale computational capability is required to achieve understanding of the role of feedback in the control and understanding of complex reactions. The usual techniques involve solution of large sets of coupled differential equations which requires considerable computational power.

- Critical Phenomena: Critical point phenomena in chemistry may now be tractable by computational means. Included in these would be the molecular ordering in liquid crystals, ferroelectric transitions and magnetic transitions.

- Crystal Growth: Problems such as those associated with the Czrochralski crystal growth process can be addressed by computational means. For example, the solution of non-linear Navier-Stokes equations have bearing on the quality or perfection of large Si crystals.

- Simulation: There are a number of problems where computer simulation can payoff. One example is studies of nucleation phenomena. Large scale computing is necessary to permit a large enough cluster of atoms to be addressed that the simulation has some generality.

- Boundary Layers: The use of soluble polymers for drag reduction also has benefited from improved computational methods and power. The declining cost of computing power and the increased availability of supercomputers should allow further advances to be made in this area.

There are also some popular areas of activity which seem to be approaching maturity. These would include the following:

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- Turbulence and many aspects of fluid dynamics

- The effects of high pressure

In summary, there are significant opportunities in computational chemistry. Work in these areas can payoff handsomely by increasing the rate of progress in important research areas and by focusing the experimental effort in the same areas.

Response to Question #7:   Are There Any Useful Scientific/Technological Areas of High Pressure
Research To Be Pursued --- Other Than Making Diamonds?

J. L. Margrave, G. M. Whitesides, H. Ehrenreich, G. H. Vineyard, J. C. Williams, J. P. Hirth, R. M. Osgood,
H. K. Bowen, M. Dresselhaus, D. K. Ferry

There is definitely a justification for DARPA to be alert to new development in the high-pressure area and to fund research which impacts DARPA materials needs.

University research programs in high pressures are usually small and have mostly tended toward uv/vis/ir and Raman spectroscopic/x-ray studies of high-pressure phases in diamond anvil cells. (DAC) Gross-heating or cooling of DAC's and laser-heating of samples under pressure have extended the applications of the DAC techniques. Excellent low-temperature work has been done on H_2 (still not metallic at 180 GPa), N_2 (still not metallic at 130-160 GPa), on Xe (still not metallic at ~100 Gpa) and on CsI (still not metallic at ~93 GPa). Low-temperature (~2K) and high-temperature (~700°C) x-ray diffraction studies of many elements/compounds have been published. Visible/uv/ir/Raman spectra of many inorganic systems and a limited number of organic systems have been reported.

We have identified the following areas in which DARPA support of high pressure research would be appropriate:

(1) New Materials Synthesis

Diamonds and diamond-analogs, including cubic-BN, cubic AlBN, SiC, BP, GaN, and similar phases may have major significance as substrates for electronic devices. Since industrial interest is mainly at the production level for diamond and c-BN, there is still a need for exploratory research in this area, including structure/property relations and applications.

High pressure techniques have recently played an essential role in clarifying the magnitude of band offsets in superlattice structures. Band offsets give the energy differences between the valence and conduction band edges in a semiconductor heterojunction relative to their bulk values. Knowing the offset is extremely important in designing optical and electronic devices that are based on abrupt heterojunctions, since the heterojunction barrier sets the value of quantities such as threshold voltage, leakage current, etc. Despite this importance, the exact values of band offsets have remained the

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subject of intense controversy for several years; neither theorists nor experimentalists could provide a clear value of this important engineering quantity for any materials system.

Now two groups at IBM have provided unequivocal measurements of the offsets in GaAs/AlGaAs. The most extensive of these measures involves using laser-induced luminescence on a sample, under high pressure, in a diamond anvil cell (0-100K bar). The measurements are done at $7°K$. The technique involves the quenching of one luminescence band, due to energy transfer into an adjacent energy level. The levels move in and out of resonance under the influence of the cell pressure. The efficacy of this technique, plus the need for band offset information on other superlattice systems, indicates that high pressure measurements will grow in importance for basic semiconductor studies.

There are interesting new opportunities for the synthesis of new magnetic materials (FeO_2, FeO_3, etc). The exploration of ultra-high-pressure organic chemistry would also appear to be extremely promising.

(2) High-Pressure Processing of Materials

The use of hot isostatic pressing techniques for densification of ceramic powders, super-alloy powders, etc., is very important but the limits on both T and P are restrictive. The forming, curing and performances of polymers/composites at high pressures should be studied. There are also many opportunities for significant research on hydrothermal processes, e.g., the preparation of clean oxide powders for ceramic uses. We believe the high-pressure processing of materials to be ripe for significant advances.

(3) Special Problem Areas

Three special questions of possible interest to DARPA are listed:

a.) Are the underwater corrosion problems for submarines significantly accelerated by the high pressures/salty water at ocean depths? Is the reduction of light intensity a factor?

b.) Is there a need for fundamental studies of metals/ceramics when subjected to rapid heating/compression during dynamic compaction?

c.) Should one continue studies of H_2 and other materials in the search for metallic phases?

We believe the answer to all three questions is "yes" and encourage DARPA support of research in these areas.

(4) New Diagnostics And Apparatus

DARPA should be aware of new high-pressure devices/diagnostics, especially those which will extend the range of pressures achievable, the time scale for achieving, maintaining and measuring these pressures, and the volume of material which can be compressed.

Summary

High-pressure research is a viable field from which one can expect significant contributions to materials science. Although a special initiative is not recommended, there are several attractive areas suitable for funding.

Response to Question #8: Ceramic Armor. How does it work? How can we understand its behavior better? What can we do to improve its performance?

B. Budiansky, A. G. Evans, G. M. Whitesides, J. L. Margrave, J. P. Hirth, McMeeking, J. W. Hutchinson

Good ceramic armor materials tend to be very hard. Microhardness tests that produce plastic flow by dislocations show that the deviatoric yield stress S_y in compression can be as much as 6 times the corresponding flow stress in good metal armor. Such high strengths would imply superb armor performance, but only if compressional splitting, and faulting, and tensile spalling could be sufficiently inhibited in space and time during the intrusion of a projectile. The primary key to such inhibition is pressure confinement.

Deviatoric stress-strain curves in compression are sketched schematically in Fig. 1 for low, moderate, and high containing pressure p. At low p, a specimen cracks into a few large chunks. In the presence of moderate p, compressive cracks coalesce into one or more major faults, at S_2, such that the faces remain in partial contact, and the stress drops rapidly with increasing straining. But with sufficient confinement, although extensive cracking and fragmentation may occur around S_3, the stress may continue to increase up to a substantially higher value S_4 that could conceivably approach the plastic yield stress S_y, followed by a pseudo-ductile behavior involving substantial plastic flow. Accordingly, successful ceramic armor designs must incorporate techniques - such as the use of metal envelopes - that induce adequate confining pressures during the projectile intrusion process. Similar considerations dictate provisions for delaying or alleviating tensile spalling.

It is evident that increasing S_y can only improve ceramic armor performance, but the influence of S_3, the fragmentation stress, is less clear. Compressive cracking occurs by the action of localized tensile fracture, which in turn is controlled by fracture toughness. Lower toughness may well be associated with finer fragmentation, and this may be more desirable than large fragments. Paradoxically, therefore, increasing the fracture toughness of a ceramic may not improve its performance. On the other hand, when penetration resistance is dominated by tensile fragmentation, a high fracture toughness would be beneficial.

There are several routes for increased understanding of the behavior of ceramic armor that should be followed in parallel. The development of simple engineering models for penetrator-armor interaction should be pursued. Such models should be more sophisticated than the Alekseevski-Tate approach, incorporating compressive cracking processes consistent with the behavior shown in Fig. 1, but elementary enough to permit rapid preliminary design and variation of parameters. At the same time, experiments to define the rough outlines of the confined stress-strain relations should be undertaken, with at least some attention to the assessment of strain-rate effects, and rigorous large-scale code development should proceed, again with appropriate experimental underpinnings that would provide guides to the incorporation of plausible, 3D constitutive relations for fragmentation and flow. The problems are considerably more challenging than the analogous ones for metals, and code developers should not try to do everything at once. But a sober program of model development, small and large scale computation, laboratory material characterization, full scale testing and confrontation of the results with those of analysis and computation, are essential for rational, optimal armor design.

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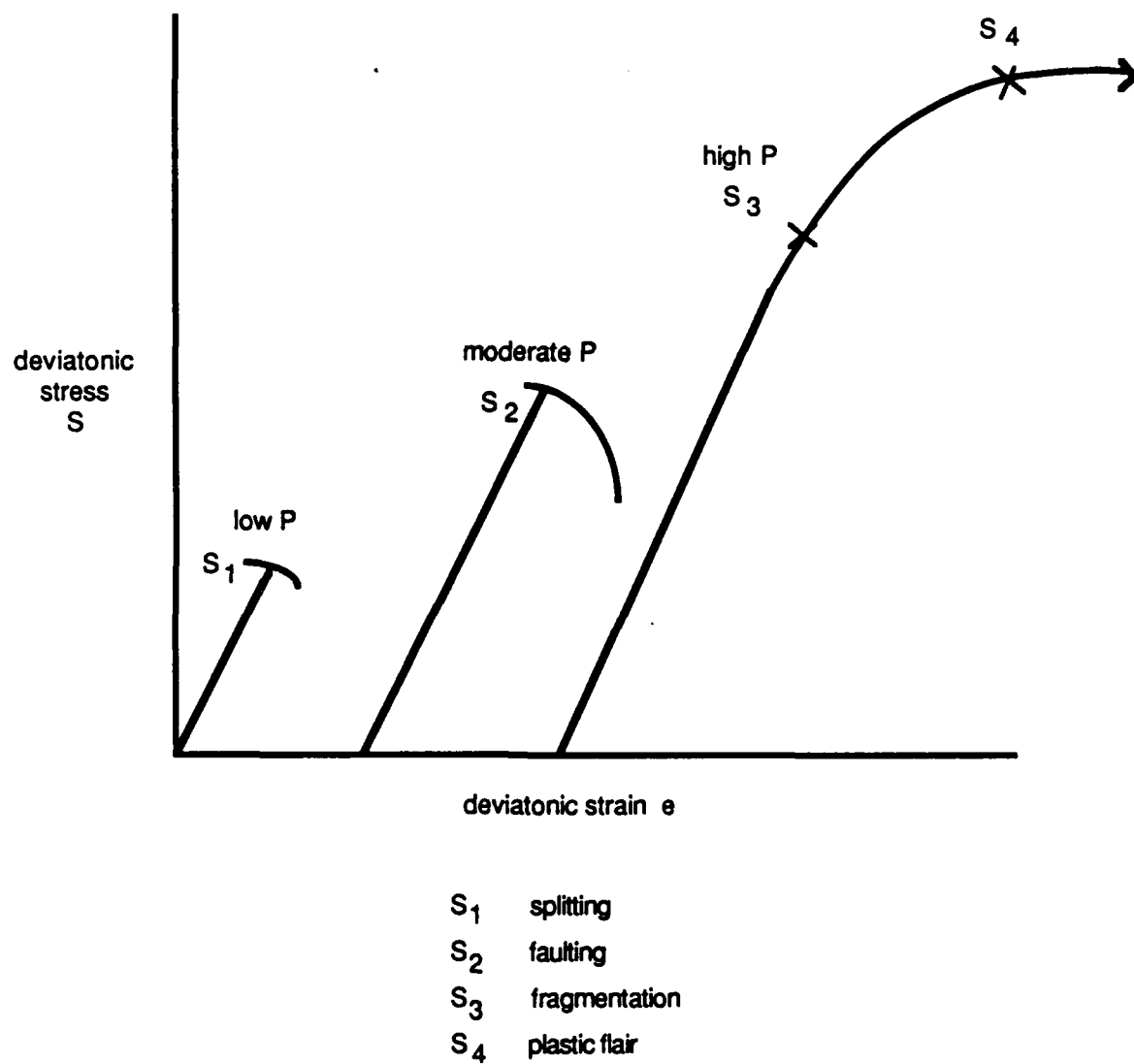|	
S_1	splitting
S_2	faulting
S_3	fragmentation
S_4	plastic flair

Figure 1.

Response to Question #9: Materials Chemistry and DARPA's Role

M. S. Wrighton

The importance of chemistry to the synthesis, processing and assembly of materials was discussed by the Materials Research Council at a special meeting held on July 25, 1986. G. M. Whitesides and John Margrave of the MRC both made informal presentations following a more formal report on an Institute for Defense Analysis study on the status and capabilities in the area of computational chemistry. The MRC participation included not only all of the chemists (Margrave, Stille, Whitesides, Wrighton) in the meeting but broad representation of the fields spanned by the MRC were active discussants (Dresselhaus, Ehrenreich, Ferry, Hirth, McGill, Osgood, Williams, Vineyard, Yariv).

Whitesides and Margrave made compelling arguments supporting the contention that the molecular perspective is an important one in addressing materials problems of technological significance where DARPA already has a stake. A non-exhaustive list of such areas include:

Molecular Precursors to Solids

Ceramics

Metals

Semiconductors

Composite Systems

Fiber Formation, Treatment

Matrix Synthesis

Microelectronics

Interfaces

Interconnects

Packaging

Materials Formed Under Extreme Conditions

Low and High Temperature Species

Plasma Chemistry

High Pressure Reactions

Energy Conversion

Non-linear Optical Materials

Biotechnology

The MRC seemed to be uniformly convinced that a molecular perspective, generally taken by ..emists, can be a useful one. However, it appears that many practicing academic chemists are not sufficiently knowledgeable concerning problems in materials technology to know how to apply their skills in addressing the important issues. Quite interestingly, the materials technology community appears to be better acquainted with where chemistry understanding is truly needed in materials than do the academic chemists. In contrast, chemists are already making major contributions in biological sciences. Considering the importance of the materials limitations in existing military systems there is a definite need to bring the skills of chemistry to the preparation, processing, and assembly of materials-based systems.

There is likely very little to be gained by announcing a contract program for chemistry per se. DARPA should continue to be responsive to research involving a chemistry perspective that addresses major materials-oriented problems. However, in addition, two specific suggestions should be given consideration: (1) Identify and hire a new DSO program manager familiar with chemistry and materials. Such an addition would add to the ability to discern genuine opportunities for research at the interface of chemistry and materials. (2) Sponsor a workshop geared to educate junior chemistry professors, early in their career, regarding the potential role for chemistry in solving materials problems. The workshop should be undertaken with the expectation on the part of DARPA and the participants that the workshop would result in new proposals with a significant prospect of funding for those which reflect high quality, originality, and relevance to the major problems in materials technology.

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